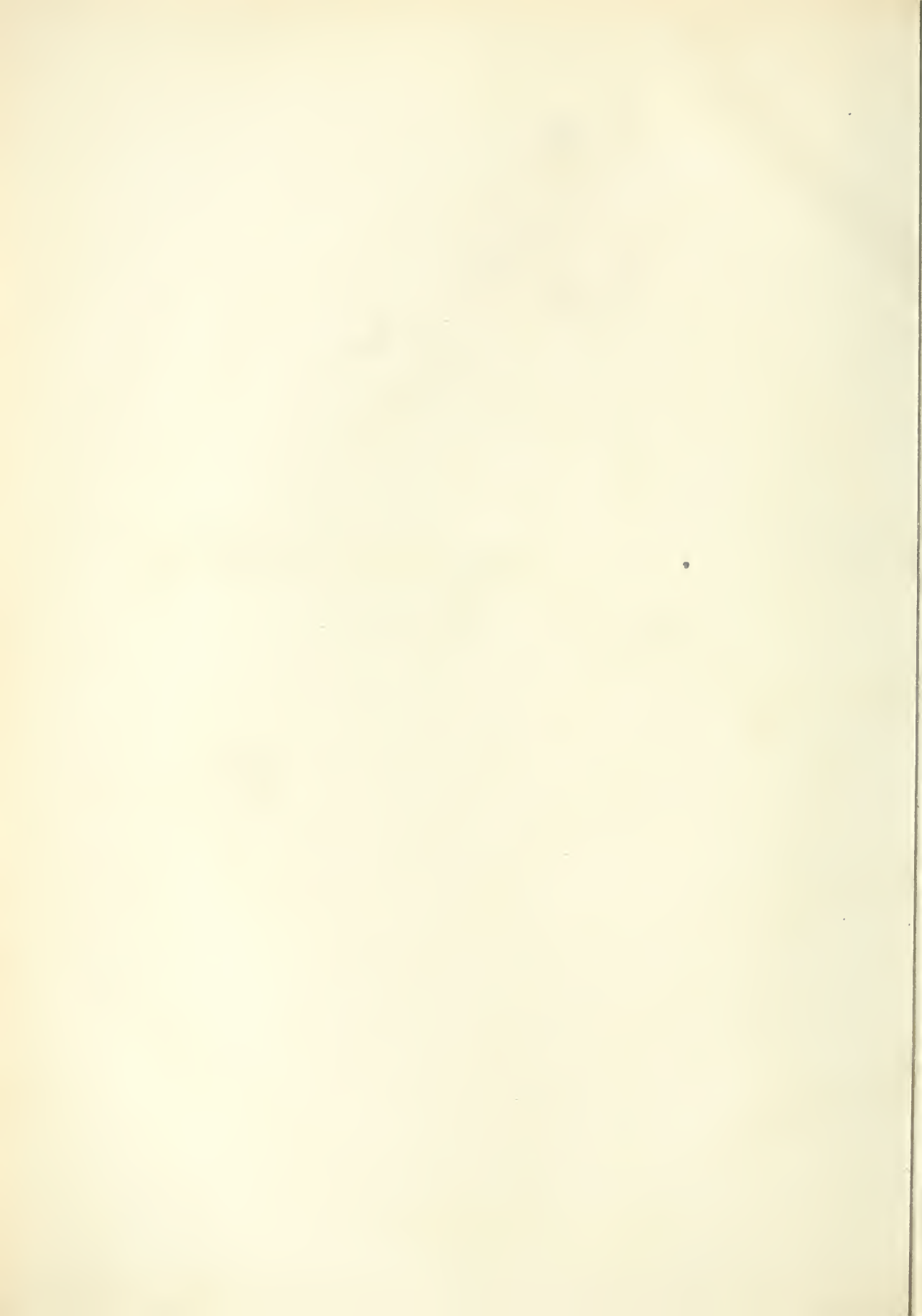


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THE CHEMICAL NEWS, JULY 11, 1902.

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

635-15-
19/1/02

VOLUME LXXXV 1902

LONDON:

PUBLISHED AT THE OFFICE, 6 & 7, CREED LANE, LUDGATE HILL, E.C.
AND SOLD BY ALL BOOKSELLERS.

MDCCCII.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,
6 & 7, CREED LANE, LUDGATE HILL,
E.C.

THE CHEMICAL NEWS.

VOLUME LXXXV.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2197.—JANUARY 3, 1902.

CONTRIBUTIONS TO THE CHEMISTRY OF CHLOROPHYLL.

No. VIII. CHANGES UNDERGONE BY CHLOROPHYLL IN PASSING THROUGH THE BODIES OF ANIMALS.*

By EDWARD SCHUNCK, F.R.S.

CONSIDERING the large quantity of food containing chlorophyll consumed by animals feeding on green herbage, it seemed to me it might be of interest to ascertain whether any, and if so what, changes are undergone by the chlorophyll of the food during its passage through the animal body.

It is stated in works on physiological chemistry that the solid excrements of animals contain chlorophyll; but this statement refers apparently to human fæces, and is certainly not correct as regards those of herbivora if unchanged chlorophyll is meant. It would indeed, *à priori*, seem very improbable that chlorophyll, after exposure at a somewhat elevated temperature to acids and other agents, such as it would meet with in its passage through the animal system, would remain unchanged, though, on the other hand, chlorophyll products of decomposition, some of which, as I have pointed out on former occasions, are very stable bodies, might be looked for in the excrements of animals.

Having treated some of the fæces of a cow that had been fed for some time on grass only, with boiling alcohol, I obtained a dark greenish-brown extract showing an acid reaction, a quantity of undigested matter consisting of stems, woody fibre, &c., being left undissolved. A little of the filtrate, on being mixed with water and shaken up with ether, gave a golden-yellow supernatant liquid, which, if chlorophyll had been present in the material used, would have shown a decided green colour, and would have exhibited the absorption spectrum of chlorophyll. In place of the latter, however, it showed the four absorption bands of phylloxanthin, as well marked, indeed, as I have ever seen them. This simple experiment proved conclusively the absence of chlorophyll, but in its place the presence of one of its products of decomposition. I have made no attempt to isolate and purify this supposed phylloxanthin, this being rendered difficult owing to the large admixture of impurities, which are chiefly of a fatty nature. The ethereal liquid just referred to would also have contained the urobilin of the fæces if present, so I imagine at least if I have rightly understood what has been stated regarding that body. The properties of urobilin, however, are not very marked. It is only by its absorption spectrum that it can with certainty be detected, but this spectrum is too inconspicuous and too faint to be

easily seen in a solution containing at the same time phylloxanthin with its dark well-defined bands, which would completely mask those of urobilin situated as these are in the same region of the spectrum. Its presence, too, if proved, would have been of little interest from my point of view, and I therefore made no attempt to establish its presence or absence.

The extract of fæces with boiling alcohol gave, after filtration and cooling, a dark coloured flocculent deposit, which was filtered off, dried, and treated with boiling chloroform. The filtered chloroformic liquid left on evaporation a quantity of purplish-blue lustrous crystals. These crystals, which are of considerable interest as regards both their properties and their origin, will be described presently. They are more readily prepared by extracting cow-dung after pressure between folds of paper with cold chloroform, filtering, and evaporating the filtrate slowly in a warm place, when the substance separates in the form of brilliant semi-metallic spangles floating in the liquid, which, after collecting and washing with alcohol, have the appearance of a lustrous crystalline mass. From the brilliancy of its appearance an observer might easily be deceived as regards its quantity, which is not really large. I have, however, obtained sufficient to enable me to determine its chief properties, and to justify the conclusion that it is a derivative of chlorophyll closely resembling, though not identical with, phyllocyanin, as I shall presently show.

For such as wish to prepare this substance, I may state, as the result of my experience, that it can only be obtained from the fæces of cows or other herbivora that have been fed exclusively on grass or other green vegetable food; those of stall-fed cattle, nourished as they usually are to a great extent with oilcake, yield none, on account perhaps of the large amount of fatty matter present in that case in the fæces. I may add that the solid excrements of sheep that have been at pasture for some time and living on herbage only, on being treated as above described, yield the same substance, but I have made no experiments with the fæces of other herbivora. I imagine that the yield of this peculiar substance is greatest from material collected in spring or early summer, but this, if correct, may be due to other causes than difference of season.

This substance not having, so far as I can ascertain, been previously observed, I propose to call *Scatocyanin*, a name kindly suggested to me by Professor Wilkins, of Owens College. Its chief properties are as follows:—Under the microscope it appears in the form of thin rhombic plates or elongated flat prismatic crystals, which are pale brown by transmitted light, of a purplish-blue colour with a brilliant metallic lustre by reflected light. When heated between watch-glasses it is decomposed without melting or swelling much or yielding any subli-

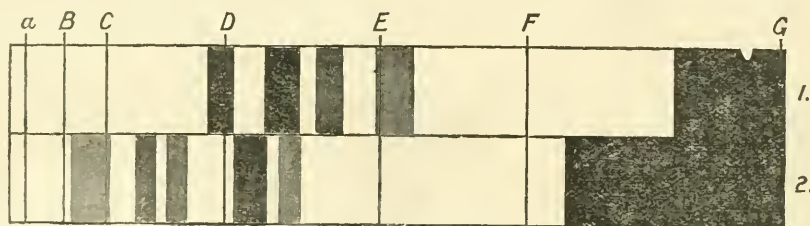
* A Paper read before the Royal Society, December 12, 1901.

mate; heated further on platinum, it burns away, leaving a little ash. It is [almost insoluble in boiling alcohol, ether, carbon disulphide, and benzol, but it dissolves, though not readily, in chloroform, giving a solution which shows an absorption spectrum of five bands, almost identical with those of phyllocyanin. It dissolves in boiling glacial acetic acid, giving a fine crimson solution, which, when sufficiently dilute, shows an absorption spectrum of four bands—of which the two first are well defined, the third faint with some obscuration between it and the second band, the fourth band also faint and not well defined (see Fig.) From a saturated solution in boiling acetic acid the substance separates on cooling and standing in lustrous purplish-blue needles.

It dissolves in concentrated sulphuric acid with a brilliant grass-green colour, which, on standing, changes to purplish-blue. The solution now shows a characteristic absorption spectrum of five bands, of which the first and fifth are faint and poorly defined, the second and third well defined, but the fourth only moderately so, while there is much obscuration between the fourth and fifth bands, with just a trace of a sixth band in the green between the fifth band and the total obscuration (see Fig.)

The sulphuric acid solution on being mixed with several times its volume of water changes its colour from purplish-blue to a fine purple without giving any precipitate, and

so prepared:—When dry it has the appearance of a dull red mass of crystalline needles. Heated on platinum, it melts easily to a brown mass, solidifying again on cooling; on further heating, it gives off red fumes, and burns away, leaving no ash. When heated in a test-tube or between watch-glasses, it gives a small quantity of amorphous brown sublimate with a few crystalline needles. It dissolves in boiling alcohol, giving a bright yellowish-red solution, which, on cooling, deposits crystalline needles, becoming almost colourless. It is moderately soluble in ether, benzol, and glacial acetic acid; very soluble in chloroform. The chloroformic solution shows no absorption bands, only obscuration in the blue. It is quite insoluble in caustic potash liquor, even on boiling. It dissolves in concentrated sulphuric acid, giving a dull red solution, which, after the addition of a considerable quantity of acid, shows no absorption bands, only obscuration in the blue and green; on the addition of water, the solution turns reddish-yellow without giving any precipitate, but on standing for a short time the colour turns to a fine violet, and then shows a broad ill-defined absorption band between the red and green. Not showing any very characteristic reaction but the one last mentioned, it must remain doubtful how and where it originates. It may possibly be a constituent of the green parts of plants not hitherto observed, though I believe it myself to be a



ABSORPTION-SPECTRA OF SCATOCYANIN SOLUTIONS.

1. Scatocyanin in glacial acetic acid. 2. The same in concentrated sulphuric acid.
(These spectra were mapped by my son, Charles A. Schunck).

without showing any change in its absorption spectrum. On standing, however, for some time the liquid becomes nearly colourless, and deposits rosettes of lustrous crystalline needles, presumably of unchanged substance; so that it appears no sulphonic acid is formed in this reaction, the colour of the solution in sulphuric acid being due probably to a loose combination of the substance with the acid. The substance is soluble in boiling aniline; the solution is dull red, and gives with alcohol a deposit of brilliant needle-shaped crystals, the filtrate from which shows the same spectrum as the solution in acetic acid. The substance is insoluble in aqueous caustic potash, but dissolves in alcoholic potash, giving a yellow solution.

There is another substance of definite character, and assuming a crystalline form which I have obtained, though not always, along with the preceding. Having treated the fæces of a cow that had lived for some time on green vegetable food, with acidulated alcohol (seventeen parts of rectified spirit to three of sulphuric acid, the mixture prescribed for the preparation of so-called stercobilin), I added water to the filtered extract, and shook up with chloroform. The chloroformic liquid after separation was evaporated, when it left a brown syrup. This, treated with boiling alcohol, dissolved in part, a semi-crystalline pink residue being left undissolved, which, after separation, was found to be soluble in boiling acetic acid with a crimson colour, and consisted doubtless of scatocyanin. A further quantity of this was deposited on again evaporating; on further evaporation, the filtrate left a thin brown syrup which was mixed with a large quantity of alcohol. On standing, a voluminous crystalline deposit separated, which was filtered off, and slightly washed with alcohol.

The following are the chief properties of the substance

derivative of chlorophyll—meaning by chlorophyll the ensemble of the colouring matters of green leaves—formed by some unknown process in the animal economy, but the fact of its solutions showing no absorption bands does not lend countenance to this view. Having also observed it on one occasion only, I do not feel justified in giving it a name, or in placing it in any known category of vegetable or animal colouring matters.

Another constituent of the fæces remains to be mentioned. It was referred to above as showing in solution the absorption spectrum of phylloxanthin. After all the substances capable of assuming a crystalline form have been separated from the alcoholic extract of the fæces, this phylloxanthin-like substance is found in the final mother-liquor. I have not succeeded in obtaining it in a crystalline or any other definite form, on account probably of the large quantity of fatty matter with which it is associated; but there is no reason, I think, to suppose that it differs essentially from the phylloxanthin described in previous communications as a product of the action of acids on chlorophyll.

The conclusions to which the experiments above described lead may be summarised as follows:—

1. The fæces of animals supplied with green vegetable food only—such at least as have so far been examined—contain no chlorophyll, but in its place substances which must be supposed to be derivatives of chlorophyll, formed partly by the action of acids on the chlorophyll of the food, partly by some agency to which the latter is subjected in its passage through the body.

2. Of these substances, one seems to be identical with phylloxanthin, a well known product of decomposition of chlorophyll. Another is a substance of well-marked properties, nearly resembling, but not identical with,

phyllocyanin. It has not, so far as my experience goes, been hitherto observed as a result of any process of decomposition to which chlorophyll has been subjected outside the animal body. I consider it as a body *sui generis*, characterised by its fine purplish-blue colour and its brilliant metallic lustre. The existence of other products in addition to these two is possible. On one occasion, indeed, a definite crystalline substance was obtained, which seemed to be peculiar, but that it was in any way connected with chlorophyll could not with certainty be maintained.

NOTE ON THE SESQUITERPENE OF EUCALYPTUS OILS.*

By HENRY G. SMITH, F.C.S.,
Assistant Curator, Technological Museum.

IN this paper the author showed that a sesquiterpene occurs in many Eucalyptus oils, and that it is this constituent that gives the pink colouration to Eucalyptus oil when testing for eucalyptol with phosphoric acid. In the oil of *E. haemastoma* the sesquiterpene occurs in large amount, over 50 per cent of the crude oil distilling above 255° C. It is also present in quantity in the oils of several other species. Crystallised chemical products could not be obtained with it by the methods used. It is characterised by a range of five colour reactions which it gives with acids and with bromine when dissolved in glacial acetic acid. When the vapour of bromine is allowed to fall into the tube containing such a mixture, immediately it touches the liquid a crimson colour is formed, quickly changing to violet, and finally to a deep indigo-blue. It boils under atmospheric pressure at 260–265° C., has a specific gravity 0.9249 at 19° C., as obtained by repeated fractional distillation finally over sodium. Combustion results gave the terpene formula, and a vapour density determination showed it to be a sesquiterpene. The name *Aromadendrene* has been proposed for it.

BISMUTH ASSAY.

By A. W. WARWICK and T. D. KYLE.

OWING to the high price paid for bismuth, persistent search is being made for that metal; the result is that the localities in which it is known are rapidly increasing, especially in Colorado. In Leadville alone it is safe to say that nearly every mine has some bismuth in it, although few mines have ore rich enough to ship as bismuth. Most of the assay manuals give but scant attention to the bismuth assay, and the methods given are either inaccurate, or clumsy and laborious. For example, Furman's Manual gives a combined fire and gravimetric method which he admits to be inaccurate, but claims to be accurate enough for all technical purposes. We find that this method is not correct to within 0.75 per cent and that error amounts to 11.25 dol. per ton on a 10 per cent ore—an error too great for any good commercial work. It is also very laborious, taking from two to three hours to perform, which is a very serious objection in an ordinary assay office. Beringer's text-book gives the usual gravimetric method as well as a fire assay, remarking that the volumetric methods offer no advantages over the gravimetric method.

The fire assay is notoriously inaccurate, and the gravimetric method usually followed is too slow; we believe, therefore, that an account of a simple volumetric assay which is accurate will be of interest. It may also help to prevent those annoying disputes between buyer

and seller which occur owing to differences in assay methods.

The price paid for bismuth is quite high, varying from 15 dol. to 20 dol. per unit per ton according to market price for bismuth, grade and quality of ore; an error, therefore, of 0.1 per cent amounts to from 1.50 dol. to 2 dol. per ton, showing that any bismuth assay should be very accurate. A good method of assay for bismuth is a desideratum, and it should not only be accurate, but simple and rapid, and also, if of the volumetric order, the standard solution used should be reasonably permanent. The writers have found these conditions fulfilled by a modification of the process devised by Pattison Muir some years since. It is rapid, 40 minutes sufficing to complete a determination. It is accurate, results agreeing to within 0.1 per cent with ordinary care; with extreme care results agree to within 0.05 per cent. It is simple; no delicate manipulations are required. The standard solution is the inevitable potassium permanganate; the usual standard solution used in the iron determinations can be used (1 c.c. = 0.010 gm. Fe), although for very accurate work a dilute solution is better. A permanganate solution in which 1 c.c. = 0.010 gm. Fe, will be equal to 0.0186 gm. bismuth; by diluting 100 c.c. of this with 86 c.c. of water a solution of permanganate will be obtained of which 1 c.c. should equal 0.010 gm. of bismuth. A permanganate solution 1 c.c. = 0.010 gm. Fe; found = 0.01868 gm. Bi. 100 c.c. permanganate above + 86 c.c. of water; 1 c.c. found = 0.01017 gm. Bi.

The process consists of the following operations:—(1) Solution in nitric acid, (2) precipitation as bismuth-oxalate, (3) conversion of the normal oxalate into basic-oxalate by boiling with water, (4) solution of the basic bismuth oxalate, (5) titrating the hot solution with potassium permanganate.

Before recommending this process the writers have investigated the influence of metals upon the accuracy of the assay and the influence of the variation of conditions. At the outset we found that the solution of the basic-oxalate in hydrochloric acid gave a very erratic end-point, and that the solution of basic-oxalate in sulphuric acid was too slow and gave a low result. We therefore used hydrochloric acid to dissolve the oxalate, neutralised with ammonia, and made quite acid with dilute sulphuric acid. This simple modification results in the titration being as direct and clear as an ordinary iron assay: one-half of one drop, or 0.05 c.c., showing the end-point.

We conduct an assay as follows:—

1. One gm. of the finely crushed pulp is attacked with 5 to 10 c.c. concentrated nitric acid, in a casserole covered with a watch-glass and evaporated to dryness on the hot plate. To the residue is added 5 c.c. nitric acid and the casserole replaced on the hot plate for a few minutes, breaking up the mass with a glass rod. We formerly filtered off the insoluble residue, but found it quite unnecessary. To the mass in the casserole 25 c.c. of water are added, and the contents emptied into a beaker and made up to about 100 c.c. with hot water.

2. To the bismuth solution 5 grms. of ammonium oxalate or oxalic acid are added and the whole boiled vigorously for five minutes. The beaker is removed from the hot plate, and in a minute or two the precipitate will completely settle. The supernatant is filtered off; with a rapid filter this is accomplished about as quickly as the liquid can be safely poured out of the beaker. The precipitate should be left as much as possible in the beaker.

3. The precipitate is boiled with two successive quantities (about 50 c.c.) of water; filtering through the same filter used in (2). These two boilings should entirely convert the bismuth oxalate into the basic salt when an ordinary ore of 10 per cent is being assayed. Should, however, the filtrate be acid to litmus-paper, boiling is continued until the final filtrate is neutral.

4. The basic oxalate on the filter is washed down to the point and 2 to 5 c.c. hydrochloric acid (1 acid to 1 water) are added, and the filtrate caught in the beaker containing

* A Paper read before the Royal Society of New South Wales, November 6, 1901.

the basic oxalate precipitate; the filter is washed with water twice. The basic oxalate is entirely dissolved by gentle warming. When entirely dissolved the solution is made up to 250 c.c. with hot water.

5. The hydrochloric acid in solution is neutralised with ammonia, about 2 c.c. should suffice. The resulting precipitate is re-dissolved by the addition of sulphuric acid (1 acid to 4 water) and an excess of a few c.c. added.

6. The solution is titrated at a temperature of from 70° C. to 100° C. The reaction between the oxalic acid and the permanganate is slow at first, but is instantaneous after a few drops have been added; the addition of permanganate is continued to a faint rose tint.

Precautions.—Insufficient nitric acid present in solution, before the addition of oxalate (operation 2), will result in the partial precipitation of the bismuth as basic nitrate and a low result will be obtained. Too much nitric acid must not be present; the deleterious effects of too much nitric acid can be obviated by adding a large amount of water. The bismuth oxalate must be entirely converted into basic oxalate or the results will be high. The normal oxalate is readily converted into the basic salt by repeated boilings with fresh quantities of water. When the filtrate is neutral to litmus-paper the reduction is complete. For the ordinary ore of 10 per cent two boilings generally suffice. The solution of the basic oxalate before titration must be perfect or the result will be low. Hydrochloric acid must not be used in dissolving up the ore. Nitric acid completely effects the solution of the bismuth in the ore.

Interferences.—Lead, iron, copper, zinc, arsenic, tellurium have no effect on the assay.

Some results obtained are as follows:—

Test Bismuth ore—

1. Found 9.6% gravimetric, 9.58% volumetric.		
2. " 4.49% " 4.49% "		
3. " 10.30% " 10.32% "		
	Grms.	Grms.
4. 0.500 Bi containing 0.5 Pb	Found 0.5010 Bi	
5. 0.500 " " 1.0 Pb	" 0.4968 "	
6. 0.500 " " 1.0 Cu	" 0.4987 "	
7. 0.500 " " 1.0 Zn	" 0.4994 "	
8. 0.500 " " 0.7 Fe	" 0.5010 "	
9. 0.500 " " 1.0 As ₂ O ₃	" 0.4993 "	
10. 0.500 " " 0.5 Sylvanite	" 0.5001 "	

These results show that the method is quite accurate and suitable for all ordinary commercial work. Bismuth ores are, as a rule, quite free from large amounts of impurities, but the method is applicable to even very impure ores. By having an ample supply of hot water on hand the assay can be conducted very rapidly; half-an-hour will, as a rule, suffice to complete the assay; certainly no more than forty minutes will be required.—*Engineering and Mining Journal*, April 13, 1901.

ON THE RELATION OF THE VISCOSITY OF MIXTURES OF SOLUTIONS OF CERTAIN SALTS TO THEIR STATE OF IONISATION.*

By JAMES BARNES, B.A., Dalhousie College, Halifax, N.S.

THE present paper is the result of a piece of work undertaken at the suggestion of Prof. MacGregor, for the summer vacation of 1899, the object being to find out in the case of mixtures of aqueous solutions of certain electrolytes with a common ion, whether or not it is possible, by the aid of the dissociation conception, to predict the viscosities of the mixtures, when sufficient data as to the viscosities and conductivities of the constituent solutions are available.

The salts selected were sodium chloride, potassium chloride, barium chloride, sodium sulphate, potassium sulphate, and copper sulphate, the viscosities of simple solutions of these salts having been determined by Reyher (*Zeit. f. Phys. Chemie*, 1888, ii., 774), and Wagner (*Ibid.*, 1890, v., 31), and that of mixtures of them by Kanitz (*Ibid.*, 1897, xxii., 336), and extensive series of observations on the conductivity by Kohlrausch and by former students of Dalhousie College, being available. As will be seen below I found Kohlrausch's values of the conductivity sufficient for my purpose (Kohlrausch u. Holborn, "Leitvermögen der Elektrolyte," 1898, pp. 159, 160, tab. 2).

Professor MacGregor (*Trans. N. S. Inst. Sci.*, 1896-1897, ix., 219) has pointed out that, both on theoretical grounds and because of the way in which the ionisation coefficients and such physical properties as specific gravity, viscosity, &c., in general, vary with the concentration in simple solutions, it is to be expected that the value of any such property, for a simple solution which is so dilute that the dissociated and undissociated molecules may be regarded as without mutual action, will be expressed by the formula:—

$$P = P_w + k(1-a)n + lan \dots (1)$$

where P is the numerical value of the property for the solution, P_w that of the same property for water under the same physical conditions, n the concentration expressed in gramme-equivalents per unit volume, a the ionisation coefficient of the electrolyte in the solution, and k and l constants, called ionisation constants.

He has further shown that the value of a property for a mixture of two electrolytes will be given in terms of the values of the ionisation constants as determined for the simple solutions, by the expression:—

$$P = P_w + \frac{1}{\phi} \left[\left(k_1(1-a_1)n_1 + l_1a_1n_1 \right) \frac{v_1}{v_1+v_2} + \left(k_2(1-a_2)n_2 + l_2a_2n_2 \right) \frac{v_2}{v_1+v_2} \right] \dots (2)$$

where the n 's are the concentrations of the constituent solutions (the electrolytes being indicated by 1 and 2), the a 's the ionisation coefficients of the respective electrolytes in the mixture, the v 's the volumes of the constituent solutions, and ϕ the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions.

The application of the first expression to simple solutions is, as Prof. MacGregor has shown (*Trans. N. S. Inst. Sci.*, 1898-99, x., 61, footnote), of little theoretical interest; but that of the second to mixtures, because of its being based on the dissociation theory and involving no arbitrary constants, is of very considerable interest. It is the applicability of this expression (2) that the present paper is intended to test with mixtures of solutions of the above-mentioned salts.

The observations of Reyher, Wagner, and Kanitz were made on somewhat stronger solutions than those for which the above expressions might be expected to hold, but they were considered as probably sufficiently dilute to warrant the expectation of an approximate applicability of the expressions.

Simple Solutions.

For the determination of the ionisation constants in expressions (1) and (2), one must know the ionisation coefficients for the four solutions examined in the case of each salt by Reyher and Wagner. Unfortunately all the observations on the viscosity of these salts were made at 25° C., while all the available conductivity data, from which the ionisation coefficients are obtained, were at 18° C., and thus it was necessary either to reduce the viscosity values from 25° to 18° or the conductivity values from 18° to 25°. This latter reduction was carried out, as data for the former were not available. This involved

* Transactions of the Nova Scotian Institute of Science, x., p. 113.

much work; because for the determination of the ionisation coefficients at 25°, it was necessary to obtain both the specific molecular conductivity at 25° and the specific molecular conductivity at infinite dilution for 25°.

Determination of the Specific Molecular Conductivity at Infinite Dilution for 25° C.

The value of the specific molecular conductivity at infinite dilution for 25° for each salt was obtained from Kohlrausch's value at 18° (Kohlrausch u. Holborn, *loc. cit.*, p. 200, tab. 8), by aid of Déguisne's data (*Ibid.*, p. 195, tab. 7). These data were employed in obtaining the specific molecular conductivity at 25° from the values at 18°, for the three weakest solutions given in Kohlrausch's and Déguisne's tables (*Ibid.*, pp. 159, 160, tab. 2); and the ratio—

$$\frac{\mu_{25} - \mu_{18}}{\mu_{18}}$$

was then determined, where μ_{25} and μ_{18} are the specific molecular conductivity at 25° and 18° respectively.

Table I. gives the values thus obtained. The concentrations are expressed in gramme-equivalents per litre, and the specific molecular conductivities in terms of this unit and of 10^{-4} times, Kohlrausch's new unit of conductivity ($\text{ohm}^{-1} \text{ cm.}^{-1}$) (*Ibid.*, p. 1).

TABLE I.

Concentration.	Sp. mol. cond. at 18° C. (μ_{18}).	Sp. mol. cond. at 25° C. (μ_{25}).	$\frac{\mu_{25} - \mu_{18}}{\mu_{18}}$
NaCl.			
0.0005	1085	1262	0.163
0.0002	1092	1270	0.163
0.0001	1097	1276	0.163
KCl.			
0.0005	1283	1484	0.156
0.0002	1291	1494	0.157
0.0001	1295	1499	0.157
$\frac{1}{2}$ BaCl₂.			
0.0005	1183	1375	0.162
0.0002	1198	1394	0.163
0.0001	1205	1402	0.163
$\frac{1}{2}$ K₂SO₄.			
0.0005	1308	1516	0.159
0.0002	1327	1540	0.160
0.0001	1335	1549	0.160
$\frac{1}{2}$ Na₂SO₄.			
0.0005	1083	1266	0.169
0.0002	1096	1281	0.169
0.0001	1105	1292	0.169

As the ratio—

$$\frac{\mu_{25} - \mu_{18}}{\mu_{18}}$$

was thus found to be constant for the two most dilute solutions of every salt, and as these solutions are very dilute, this ratio may be assumed to approximately hold for infinite dilution. Observations on the conductivity of weaker solutions at different temperatures were not at hand; and the writer used the value of this ratio for the solution of concentration 0.0001 for the calculation of the specific molecular conductivity at infinite dilution for 25° C.

The following Table II. gives the values of the specific molecular conductivity at infinite dilution for 25° C. as thus obtained from the values at 18° C. In the case of copper sulphate this method could not be employed for want of data. A somewhat doubtful value obtained by Bredig, was therefore used (*Zeit. f. Phys. Chem.*, 1894, xiii., 220). The conductivities are expressed as in Table I.

TABLE II.

Electrolyte.	Specific molecular conductivity at infinite dilution.	
	18° C.	25° C.
NaCl	1103	1283
KCl	1312	1519
$\frac{1}{2}$ BaCl ₂	1232	1433
$\frac{1}{2}$ K ₂ SO ₄	1350	1566
$\frac{1}{2}$ Na ₂ SO ₄	1141	1334
$\frac{1}{2}$ CuSO ₄	—	1423

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extraordinary General Meeting, December 12th, 1901.

Prof. EMERSON REYNOLDS, Sc.D., F.R.S., President, in the Chair.

THE PRESIDENT stated that this meeting had been convened in accordance with a requisition signed by 128 Fellows of the Society, and that the following motions would be proposed:—

(1). On line 7 of By-law XI. (page 21, fifth line from top) to delete the words "the Council," and insert in their place the words "an Extraordinary General Meeting of the Society."

(2). To resolve that the Ordinary Meetings of the Society shall continue to take place, as heretofore, on Thursdays at 8 p.m.

Motion (1) was proposed by Mr. HEHNER, and seconded by Mr. PAKES.

Prof. FRANKLAND proposed, and Prof. RAMSAY seconded, the following amendment:—

"That this meeting desires to express its continued confidence in the Council as the Executive of the Society, as it has no reason to doubt that all the business of the Society, including the selection of days and hours of meeting, will be managed as heretofore in the interests of the Society as a whole and in accordance with the wishes of the majority of the Fellows."

After a discussion in which the following Fellows took part:—Dr. Divers, Mr. A. H. Allen, Mr. D. L. Howard, Professor Smithells, Dr. Lewkowitsch, Professor Dewar, Professor Warrington, and Mr. Phipson Beale, K.C., the PRESIDENT asked for a show of hands, and declared the amendment carried. A poll having been demanded, the PRESIDENT announced that it would be taken by means of cards having "For" and "Against" printed on them, with a space for the signature of the Fellow voting, one of these words to be deleted. Mr. Heycock, Dr. Hewitt, Dr. Shields, and Dr. Travers, having been appointed scrutators,

The PRESIDENT announced that the votes were—For the amendment, 128; against, 120.

The PRESIDENT then declared the following carried:—

"That this meeting desires to express its continued confidence in the Council as the Executive of the Society, as it has no reason to doubt that all the business of the Society, including the selection of days and hours of meeting, will be managed as heretofore in the interests of the Society as a whole, and in accordance with the wishes of the majority of the Fellows."

Ordinary Meeting, December 19th, 1901.

Prof. J. EMERSON REYNOLDS, F.R.S., President, in the Chair.

Messrs. Kiddell, Larter, Harding, and H. C. T. Gardner were formally admitted Fellows of the Society.

The SECRETARY read the following Address which was presented on November 24th to Professor Berthelot in the name of the Chemical Society by the President, who was accompanied by Dr. Gladstone and Professor Ramsay, as the representatives of the Society:—

To M. MARCELLIN BERTHELOT, Senator, late Minister for Foreign Affairs, Member of the Institute.

SIR,—On behalf of the President, Officers, Council, and Fellows of the Chemical Society, we beg to offer you, the Senior Foreign Member of our Society, our heartiest congratulations on the occasion of the Fiftieth Anniversary of your first scientific publication.

The Chemical Society has recently received the first volumes of your monumental work, yet to be completed, including the great number of papers which you have contributed, during fifty years of scientific activity, to the Chemistry of the hydrocarbons, and their methods of formation.

There is, however, scarcely any department of Chemical Science in which you have not worked as a pioneer with distinguished results, whilst to you is largely due the foundation of a new branch of the Science, namely, Thermo-Chemistry.

Alike in the history of our Science, and in its applications to Agriculture and Industry, you have made brilliant contributions.

We trust that for many years you may possess the health and strength to continue those investigations which have made your name famous throughout the Scientific world.

Signed, on behalf of the Chemical Society,

J. EMERSON REYNOLDS, President.

WILLIAM A. TILDEN, Treasurer.

WYNDHAM R. DUNSTAN, } Secretaries.

ALEXANDER SCOTT, }

RAPHAEL MELDOLA, Foreign Secretary.

November 22nd, 1901.

Day and Hour of Meeting.

The PRESIDENT announced that at the Meeting of Council held this afternoon, the following resolution was unanimously adopted:—

"That having regard to the discussion which took place at the Extraordinary General Meeting on December 12th, the Council resolves to make the experiment of holding the Ordinary Meetings, as far as possible, alternately at 5.30 p.m. on Wednesdays, and at 8 p.m. on Thursdays, from January, 1902, until the end of the present session in June, instead of holding meetings on Wednesdays at 5.30 p.m. only during the period from January to March, 1902, as stated in the resolution of July 4th, 1901, which is hereby rescinded."

And that a Committee had been appointed, consisting of the President, the Treasurer, the Senior Secretary, Dr. Armstrong, Professor Dobbie, and Dr. Forster, to arrange the exact dates on which future meetings during the session should be held.

The next Ordinary Meeting of the Society will be held on Thursday, January 16th, at 8 p.m.

It was also announced that Sir Henry Roscoe had presented a plaster cast of the bronze portrait on Bunsen's tomb in Heidelberg, and that a photograph of a bas-relief of Professor Julius Thomsen had been presented to the Society by Mr. Harald Faber.

Certificates were read for the first time in favour of Messrs. Evelyn Andros de la Rue, 52, Cadogan Square, S.W.; Keith Benham Benham, Deans Hall, Stafford; William Dennis, Ocean Road Pharmacy, South Shields; Paul Haas, 11, Westbourne Park Road, W.; Eugene Edwin Hennessey, Bigods, Dunmow, Essex; William Holdsworth Hurlley, St. Bartholomew's Hospital, E.C.; David Smith Jardin, Rathgar House, Rathgar; Harry Lucas, 1, St. Agnes' Place, Kennington Park, S.E.;

John Ross MacKenzie, 31, Bailey Street, Ton-Pentre, Glam.; William Mantland, 236, Brookhill, Sheffield; Francis Martin, 64, Samuel Street, Woolwich; Francis Hylton Molesworth, Turrumurra, Sydney, N.S.W.; Alfred Holley Munday, 17, St. Margaret's Road, Plumstead; Robert Eley Blake Smith, 93, Upper Richmond Road, Putney, S.W.; William Southworth, County Council Farm, Hutton, Preston, Lancs.

Of the following papers, those marked * were read:—

*171. "Corydaline. Part VII. The Constitution of Corydaline." By J. J. DOBBIE, D.Sc., M.A., and A. LAUDER, B.Sc.

The decomposition products of corydaline have been studied by the authors in greater detail with the following results:—The acid, $C_6H_4N(CO_2H)_3$, obtained by oxidising corydaline (*Trans.*, 1897, lxxi., 657), is, by long-continued heating with potassium permanganate in alkaline solution, converted into 2:3:4:6-pyridinetetracarboxylic acid. The acid, $C_6H_4N(CO_2H)_3$, must therefore either be 2- CH_3 3:4:6-pyridinetetracarboxylic acid or 2- CH_3 4:5:6-pyridinetetracarboxylic acid. From what follows, the former formula is probably the correct one.

Corydic acid, $C_{12}H_6N(OCH_3)_2(CO_2H)_3$ (*Trans.*, 1897, lxxi., 657), is soluble in hydrochloric acid, and under certain conditions forms an unstable hydrochloride. When boiled with potassium permanganate, it is split up into a mixture of meta-hemipinic acid and the acid $C_6H_4N(CO_2H)_3$.

When corydic acid (*Trans.*, 1897, lxxi., 657), $C_{14}H_9N(OCH_3)_2(CO_2H)_2$, is oxidised with permanganate at the ordinary temperature, it yields a yellow, dibasic acid, $C_{12}H_9N(OCH_3)_2(CO_2H)_2$, which contains the two methoxyl groups of corydic acid.

Mild oxidising agents remove four atoms of hydrogen from corydaline and convert it into dehydrocorydaline, an intensely yellow coloured base (*Trans.*, 1897, lxxi., 657). Berberine is also a yellow coloured base, but readily takes up four atoms of hydrogen, forming colourless tetrahydroberberine. Corydaline therefore corresponds to tetrahydroberberine and dehydrocorydaline to berberine.

Corydaline (colourless).	Tetrahydroberberine (colourless).
$C_{22}H_{27}NO_4$.	$C_{20}H_{21}NO_4$.

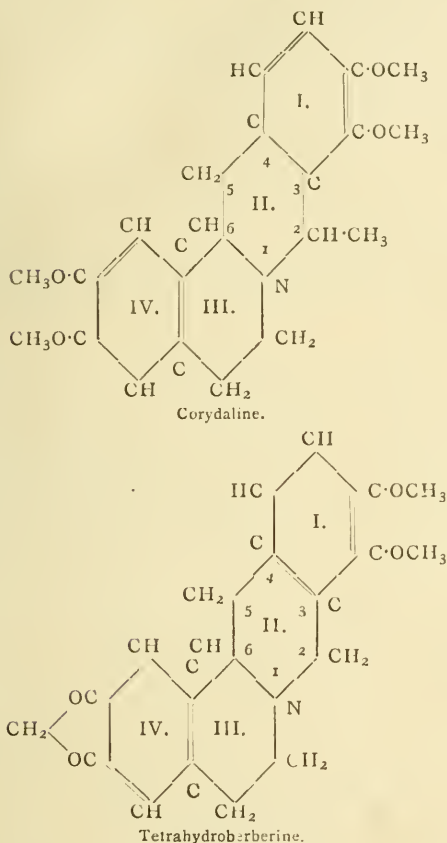
Dehydrocorydaline (yellow).	Berberine (yellow).
$C_{22}H_{23}NO_4$.	$C_{20}H_{17}NO_4$.

The four oxygen atoms of corydaline are all present in methoxyl groups (*Trans.*, 1892, lxi., 605). When oxidised with potassium permanganate at 100°, corydaline yields a mixture of hemipinic and meta-hemipinic acids, together with corydaline, $C_{11}H_{13}NO_3$, a neutral substance of which the yield is larger when the oxidation takes place at the ordinary temperature. This substance has been shown to be an isoquinoline derivative.

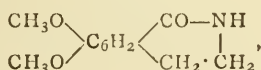
When oxidised with dilute nitric acid, corydaline, $C_{22}H_{27}NO_4$, is first converted into dehydrocorydaline, $C_{22}H_{23}NO_4$; further oxidation splits off one of the benzene rings, and yields corydic acid, a yellow, crystalline substance (*Trans.*, 1897, lxxi., 657). Corydic acid, in turn, when oxidised at 100° with permanganate, yields meta-hemipinic acid, the acid $C_6H_4N(CO_2H)_3$, and the highly insoluble, colourless corydic acid, $C_{12}H_6N(OCH_3)_2(CO_2H)_3$, which, on further oxidation with permanganate, is entirely resolved into meta-hemipinic acid and the acid $C_6H_4N(CO_2H)_3$.

As the acid $C_6H_4N(CO_2H)_3$ contains six atoms of carbon in addition to the carbon atoms of the carboxyl groups, it cannot be derived from the isoquinoline nucleus which has no methyl group attached to it, but must represent a fourth ring, and the nitrogen atom must, as in the case of berberine, be common to two rings.

There are thus four rings in corydaline. The following formula satisfactorily explains the formation of all the derivatives of corydaline which have been examined:—



By oxidation, rings I. and IV. would yield hemipinic and meta-hemipinic acids respectively; ring II., the acid $C_6H_4N(CO_2H)_3$. Corydaline,—

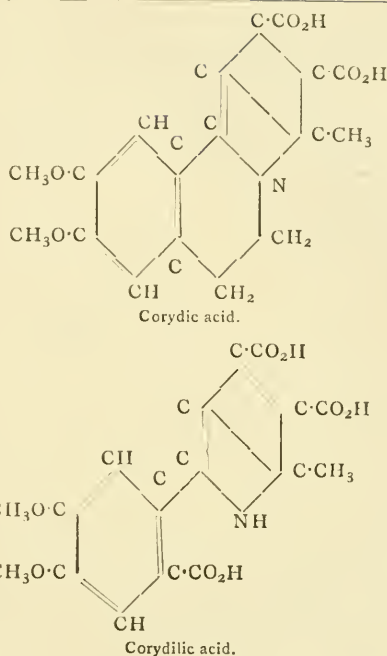


contains rings III. and IV., and would result from the oxidation of corydaline, just as ω -amidoethylpiperonyl-carboxylic anhydride results from the oxidation of berberine. Corydic acid would be formed by the destruction of ring I., and corydalic acid from corydic acid by the oxidation of ring III. The formulæ of the last-mentioned acids are therefore as given in next column.

A comparison between the formulæ of corydaline and tetrahydroberberine explains the resemblance between the two substances and their oxidation products. By oxidation, ring I., both in berberine and corydaline, yields hemipinic acid; ring IV. in berberine yields hydrastic acid, corresponding to meta-hemipinic acid from corydaline. ω -Amidoethylpiperonylcarboxylic anhydride, corresponding to corydaline, is derived from rings III. and IV., and berberonic acid, $C_5H_2N(CO_2H)_3$ [$(CO_2H)_3=3:4:6$] corresponding to the acid $C_6H_4N(CO_2H)_3$, from ring II. in corydaline.

Berberonic acid is derived from ring II., and not from ring III., which would yield carbocinchomeronic acid. This point is not dealt with by Perkin, but incidentally affords confirmation of the correctness of his formula.

The ease with which corydaline is oxidised to dehydro-corydaline is explained in the same way as in the case of the oxidation of tetrahydroberberine to berberine, the hydrogen atoms attached to the carbon atoms 2, 5, and 6 of ring II. being removed on oxidation, and a link



established between the atoms 2 and 5, and a second link between 5 and 6.

The above formula for corydaline, which accounts for its decomposition products and explains the analogies with berberine, involves the adoption of the constitution $2-CH_3:3:4:6$ for the acid $C_6H_4N(CO_2H)_3$; the alternative formula would leave the resemblance to berberine unexplained.

*172. "The Relation of Corydaline to Berberine; the Oxidation of Berberine with Nitric Acid." By J. J. DOBBIE, D.Sc., M.A., and A. LAUDER, B.Sc.

In the previous abstract it is shown that the constitution of corydaline can be expressed by a formula similar to one of the formulæ proposed by Perkin for berberine.

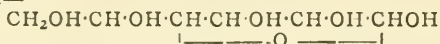
Assuming the correctness of the formula for corydaline, the absence of compounds corresponding to berberal and berberilic acid (Perkin, *Trans.*, 1890, lvii., 992) from amongst the decomposition products of corydaline, is explained, since all these substances contain an atom of oxygen united to the carbon atom 2 in ring II. (see previous abstract), where owing to the presence of the methyl group it is impossible to introduce an oxygen atom into corydaline derivatives. If the view of the relation of the two substances expressed in the formulæ is correct, the first of Perkin's alternative formulæ (Perkin, *Trans.*, 1890, lvii., 992) must be adopted. In his second formula, a double bond is shown between the carbon atoms 2 and 5 of ring II. No double bond in this position is possible in dehydrocorydaline on account of the presence of the methyl group, and the analogy between the two substances breaks down if we suppose the double bond in ring II. to occupy different positions. Whilst the absence of certain decomposition products is thus satisfactorily accounted for, the formation of corydic acid from corydaline suggests the possible formation of a similar acid from berberine. By oxidising berberine with dilute nitric acid in exactly the same way as was followed in the preparation of corydic acid (*Trans.*, 1897, lxxi., 657), an acid, $C_{16}H_{11}NO_6$ (m.p. 285°), was obtained closely resembling corydic acid in properties and obviously bearing to berberine the same relation as corydic acid to corydaline. This acid is very difficultly soluble in hot water; it dissolves in sodium

hydroxide, forming a blood red solution. It is dibasic, almost all its salts are soluble, a notable exception being the acid silver salt. It contains no methoxyl groups, hence (as in the case of corydaline) it is formed by the destruction of ring I. By oxidation with potassium permanganate, it yields berberonic acid, $C_5H_2N(CO_2H)_3$ $[(CO_2H)_3 = 3:4:6]$, and ω -amideethyl-piperonylcarboxylic anhydride. The name *berberidic* is proposed for this new acid.

*173. "The Magnetic Rotation of some Polyhydric Alcohols, Hexoses, and Disaccharoses." By W. H. PERKIN, Sen., Ph.D., F.R.S.

The object of this investigation was to see if any clue could be obtained from the magnetic rotation of the sugars as to the cause of their bi- or multi-rotation. Some of the polyhydric alcohols were also examined in order that data might be obtained from which to calculate the probable values for the various sugars.

From the rotations obtained for glucose and for fructose, it was found that the suggestion that bi-rotation was due to hydration was untenable. The magnetic rotations are too low for substances possessing the aldehydic and ketonic constitutions usually assigned to these sugars, but they correspond with substances containing an oxygen atom linked as in ethylene oxide or the lactones, all of which give low numbers. This agrees with the suggestion of Lowry (*Trans.*, 1899, lxxv., 215), that when in solution and having undergone the largest amount of change, glucose exists chiefly in an isomeric form for which he gave two formulæ, of which the more probable one, judging from the magnetic rotation, may be represented thus:—



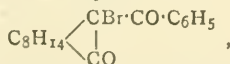
This is the formula originally proposed by Tollens for dry glucose (*Ber.*, 1883, xvi., 92). When slightly modified it can also be used to represent fructose in an isomeric condition, equally consistent with the magnetic rotation of this substance in solution.

Saccharose may be regarded as built up from glucose and fructose, both being in their isomeric forms, with elimination of water, its constitution being that proposed by E. Fischer (*Ber.*, 1893, xxvi., 2405), which is a slight modification of that suggested by Tollens (*Ber.*, 1883, xvi., 923).

Maltose and lactose, which possess both bi-rotation and reducing power, appear to have analogous structures, the formula proposed by Fischer for lactose (*loc. cit.*) being practically applicable to both, but their constitution is different from that of saccharose. Hence maltose and lactose are formed from a molecule of glucose or of galactose in the isomeric condition, plus a molecule of glucose in the ordinary or aldehydic form, minus water, the aldehydic part undergoing isomeric change to a greater or less extent when these disaccharoses are dissolved in water; in this way the possession of bi-rotation by these substances may be explained.

*174. "Stereoisomeric Halogen Derivatives of α -Benzoylcamphor." By M. O. FORSTER and Miss F. M. G. MICKLETHWAIT.

α -Benzoyl- α -Bromocamphor—

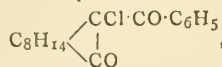


prepared by dissolving 1-hydroxy-2-benzoylcamphene in glacial acetic acid containing sodium acetate (1½ mols.) and adding a solution of bromine (1 mol.) in acetic acid, crystallises from light petroleum in large transparent, six-sided prisms, and melts at 114°; dissolved in benzene it has $[\alpha]_D = -10.0^\circ$ and in chloroform $[\alpha]_D = +10.3^\circ$.

α -Benzoyl- α -bromocamphor is formed in preponderating amount when potassium hypobromite acts on hydroxy-benzoylcamphene dissolved in potash; it crystallises from hot alcohol in transparent, rectangular plates melting at

214°, and has $[\alpha]_D = -53.2^\circ$ in benzene and $[\alpha]_D = -19.3^\circ$ in chloroform. Hydrogen bromide converts the low melting isomeride into the less readily fusible modification.

α -Benzoyl- α -chlorocamphor—

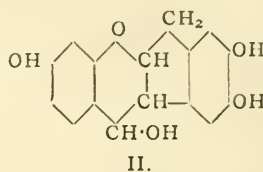
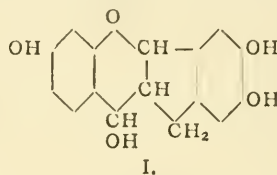


obtained by the action of sodium hypochlorite on hydroxy-benzoylcamphene, melts at 88°, and has $[\alpha]_D = -27.9^\circ$ in chloroform.

α -Benzoyl- α -chlorocamphor is produced in the same way and separated by means of its sparing solubility in alcohol; it melts at 219° and has $[\alpha]_D = +26.2^\circ$ in chloroform.

*175. "Brasilin and Hæmatoxylin. Part VI. The Constitution of Brasilic Acid of Brasilin and of Hæmatoxylin." By W. H. PERKIN, Jun.

In Part I. of this research (A. W. Gilbody, W. H. Perkin, jun., and J. Yates (*Trans.*, 1901, lxxix., 1401), it was argued that since trimethylbrasilin on oxidation with permanganate yields 2-carboxy-5-methoxyphenoxycetic acid and meta-hemipinic acid, the constitution of brasilin must be represented by one of the following formulæ:—



In order to decide between these two formulæ, the author has submitted brasilic acid to a detailed examination and has obtained results which show clearly that formula I. must be accepted as representing the constitution of brasilin.

Brasilic Acid, $C_{12}H_{12}O_6$, is produced by the oxidation of trimethylbrasilin with permanganate, but the yield is only 0.7 per cent; it is a monobasic acid, the silver salt having the formula $C_{12}H_{11}AgO_6$. The sodium salt $C_{12}H_{11}NaO_6$, is comparatively sparingly soluble and crystallises in glistening plates.

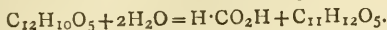
Since brasilic acid contains one methoxyl group, its formula may be written $\text{MeO}\cdot\text{C}_{10}\text{H}_9\text{O}_5\cdot\text{CO}_2\text{H}$, and as on fusion with potash it yields a substance which with ferric chloride gives a violet colouration, it is evidently derived from the resorcylic nucleus of brasilin. Furthermore, it yields an oily oxime, $\text{MeO}\cdot\text{C}_9\text{H}_8\text{O}_2(\text{C}:\text{NOH})\text{CO}_2\text{H}$, and when reduced with sodium amalgam it is converted into the lactone of dihydrobrasilic acid, $C_{12}H_{12}O_5$, which melts at 144° and is very sparingly soluble in ether.

From this behaviour, it follows that brasilic acid contains a carbonyl group, and that this is probably in the 7-position in relation to the carboxyl group.

When warmed with sulphuric acid, brasilic acid loses one molecule of water and is converted into *dehydrobrasilic acid*, $C_{12}H_{10}O_5$, a monobasic acid, which is very sparingly soluble in water, melts at 197°, and when treated with permanganate in the cold is oxidised with formation of β -methoxysalicylic acid, $\text{MeO}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$.

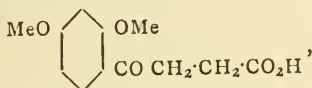
Hydroxylamine converts dehydrobrasilic acid into an oxime, $C_{12}H_{11}\text{NO}_5$, which melts at 172°. The acid, therefore, still contains a carbonyl group. When digested

with baryta water, it is readily decomposed with formation of formic acid and a new acid, $C_{11}H_{12}O_5$.

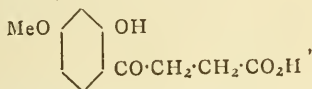


This new acid crystallises from water in colourless needles, melts at 155° , and gives, in aqueous solution, an intense violet colouration with ferric chloride; when heated with sodium methoxide and methyl iodide it yields a methyl derivative, $C_{12}H_{14}O_5$, which melts at 147° .

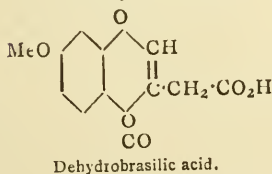
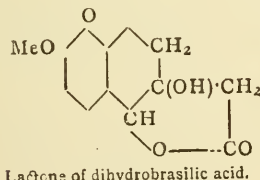
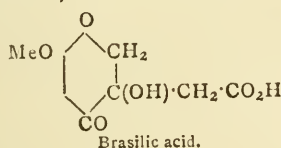
In conjunction with Mr. E. Ormerod, the author has succeeded in synthesising this latter by treating dimethylresorcinol in the presence of aluminium chloride with the ester of the half-chloride of succinic acid, $COCl \cdot CH_2 \cdot CH_2 \cdot CO_2Et$; the methyl derivative, $C_{12}H_{14}O_5$, must therefore be 2:4-dimethoxybenzoylbutyric acid—



and the acid, $C_{11}H_{12}O_5$, from which it is derived by methylation, is 2-hydroxy-4-methoxybenzoylbutyric acid—

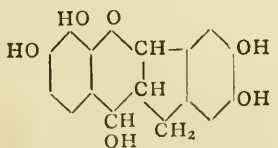


The constitutions of the other acids mentioned above are now established, and are as follows:—



Since of the two formulæ for brasilin given above, formula I. alone accounts, in a simple manner, for the formation of brasilic acid, it appears to the author that this must be accepted as representing the constitution of brasilin.

It has already been shown (*Proc.*, 1900, xvi., 107) that tetramethylhæmatoxylin, on oxidation with permanganate, gives products which are exactly similar to those obtained from trimethylbrasilin, and there can, therefore, scarcely be a doubt that the constitutional formula of hæmatoxylin is—



176. "Is Argon an Elementary Substance?" By G. MARTIN.

Some eighty distinct elementary substances are now recognised. These are assumed to be composed of dif-

ferent kinds of matter because each one has *chemical properties* peculiar to itself alone. Physical properties are of little value in deciding whether different substances are merely allotropic modifications of one kind of elementary matter, or whether they are distinct elements. The only certain test lies in the *chemical nature* of the compounds produced when the elements unite with other elements.

Elements often resemble each other so strongly in their physical nature that it is almost impossible to distinguish between them. For example, the new radio-active elements are so similar to bismuth, barium, and titanium, that many chemists still hesitate to believe them elementary. The rare earths are composed of elements so much alike that it is with the utmost difficulty they can be distinguished from one another.

But all these substances have one characteristic which stamps them as elements—each produces its own peculiar set of compounds. This characteristic is absent from argon and its companions; therefore, in order to demonstrate their elementary nature, Ramsay had to fall back on their physical properties—the most untrustworthy of all methods.

These properties stamp the new gases as a distinct class of elements; but they do not, and cannot, prove that each "element" is a single substance and not a group of closely related elements. For instance, were argon a mixture of 3 monatomic gases of like nature, and of which the atomic weights differed from each other by a fraction of a unit—as do those of nickel and cobalt—it would be impossible to distinguish the mixture from an element. It would answer to exactly the same physical tests, and could not be resolved into its compounds by any physical methods except with the utmost difficulty. It takes many thousands of fractionations to distinguish between two rare earths, which not only give different chemical compounds, but are far more unlike chemically than would be 3 monatomic inert gases.

We are peculiarly liable in the eighth group to meet with neighbouring elements of almost identical atomic weight and properties. For instance, in series 4 of the Periodic Table, as we advance with increasing atomic weight from potassium to nickel, the resemblance between successive elements steadily increases; potassium and calcium, for example, are quite unlike each other, but vanadium, chromium, manganese, and iron are all strikingly analogous, while the two last elements of the series, cobalt and nickel, have almost identical atomic weights, and resemble each other in a most remarkable degree.

In many of the other series, also, we end up in the eighth group with elements so very similar that they are classed as "triads"; for example, ruthenium, rhodium, and palladium; osmium, iridium, and platinum; the atomic weights of these triads are in every case very close together.

If each of the "elements" of Ramsay really consists of three allied substances, the eighth group of the periodic table would lose altogether its peculiar "triad" character, and split up into three distinct groups—a possibility which of late years has been running through many minds.

177. "The Action of Phosphorus Trithiocyanate on Alcohol." By AUGUSTUS EDWARD DIXON, M.D.

Lössner states in a brief preliminary note (*Zeurn. Prakt. Chem.*, 1873, [2], vii., 474) that phosphorus trichloride, acting upon an alcoholic solution of potassium thiocyanate, produces a substance crystallising in fine needles, and having the formula, $C_3H_5N_4S_4O$.

From results obtained by the author in his study of phosphorous and phosphoryl 'thiocyanates,' recently commenced (*Trans.*, 1901, lxxix., 541), it seemed probable that Lössner's compound, if really formed, must have originated through some decomposition of the phosphorus trithiotriurethane, $P(NH \cdot CS \cdot OEt)_3$, which might be expected to result from the union of phosphorus trithiocyanate, $P(SCN)_3$, or $P(NCS)_3$, with the alcohol used as

solvent; to ascertain if this was the case, the two latter substances were caused to interact directly, in presence of dry benzene.

Phosphorus trithiotriurethane could not be identified; neither could Lossner's compound; thiocyanic acid was expelled, and the residual liquid was eventually resolved into (1) an acid oil, containing phosphorus, and (2) isopersulphocyanic acid.

Phosphorus trichloride interacted violently with alcoholic potassium thiocyanate: potassium chloride was precipitated, thiocyanic acid is given off, and from the residual oily liquid, after concentration, isopersulphocyanic acid was deposited: no sign could be got of the presence of the compound $C_8H_{18}N_4S_4O$.

The author supposes the isopersulphocyanic acid, which is formed in small relative amount in either process, to be produced through the interaction of the mineral acid with the thiocyanic acid simultaneously liberated.

Benzyl alcohol interacts spontaneously with phosphorus trithiocyanate, but, as in the case of ethyl alcohol, no evidence could be obtained of the existence of a salt of phosphorus trithiotricarbamic acid, $(P(NH \cdot CS \cdot OH)_3$, if such compounds are formed at all in these interactions, it is probable that, like their congeners of the thiocarbamic class, they very readily undergo hydrolysis.

(To be continued).

NOTICES OF BOOKS.

Jahrbuch der Elektrochemie. VII. Jahrgang. By Dr. W. NERNST and Dr. W. BORCHERS. Halle a. S.: Wilhelm Knapp. 1901.

THE editors of this annual publication have to record many notable advances both in the applied and pure branches of electrochemistry. The task of summarising the progress of the science has been rendered easier owing to the many international congresses held in connection with the Paris Exhibition, where for the first time electrochemistry was allotted a place of its own among other scientific industries; these unusually favourable circumstances have induced Dr. Borchers, who is responsible for the greater part of the section of the book devoted to applied electrochemistry, occasionally to recapitulate many already known facts, so that we have in the case of some of the elements a short review of the present state of our knowledge of the various methods, both new and old, of preparing them. Wherever possible, detailed illustrated accounts of innovations in commercial processes are given for the more important elements and compounds, together with lists of German, English, and American patents, which should render the annual most useful to the inventor and the manufacturing chemist.

The year 1900 saw great progress in the application of electrochemical methods to the preparation of organic bodies, by which means many already known substances are prepared more easily than by purely chemical methods, and also various new substances have been obtained. More important, perhaps, is the extension of electrical methods of reduction and oxidation which lead to most interesting results. The section of the book devoted to organic chemistry contains accurate and full accounts of all that has been done in this respect, especially with regard to the reduction of aromatic nitro-bodies, on which Haber and Sonneborn, amongst others, have done much research.

Two indexes are given, besides lists of publications of the year 1900 in chemistry and allied subjects, and the book is well illustrated. In view of the increasing importance of electrochemical methods of preparation, such an annual as this should prove a valuable book of reference for the physical chemist and the advanced technical student.

Annuaire Pour l'an 1902. Publié par le Bureau des Longitudes. Paris: Gauthier-Villars.

WE have received this annual for 1902. It is a small compact volume containing a large amount of matter which will be very useful both to the engineer and the student of science. Among the notices included in the volume we may especially direct attention to that of M. Cornu on "Polyphase Currents," that of M. Poincaré on "Telegraphing without Wires," and that of M. Guyou on "The Decimal Division of the Circumference." The volume is in 16mo, and contains about 850 pages. It is furnished with a good index, as well as a complete table of contents. The price is 1fr. 50c.

OBITUARY.

SIR HENRY GILBERT.

IT is with great regret that we record the death of Sir Henry Gilbert, the well-known agricultural chemist, which occurred on December 23rd, 1901, at his residence at Harpenden, St. Albans.

Sir Henry was born at Hull in 1817, and was the son of the Rev. Joseph Gilbert. Shortly after leaving school he was the victim of an accident from a shotgun, which destroyed the sight of one eye, besides impairing his health for some time. Later on, he went to Glasgow University, where he made chemistry his principal study; thence he proceeded to University College, London, under Professor Graham. He also worked in the laboratory of Dr. A. T. Thomson, where he met his future collaborator, John Bennet Lawes. He next went to Germany to the University of Giessen, under Liebig, and there he took the degree of Ph.D. On returning to London in 1840 Dr. Gilbert went as assistant to his old teacher, Professor A. T. Thomson, at University College.

In the year 1843 he became associated with John Lawes, and assumed control of the chemical laboratory at the Rothamsted Experimental Station, Harpenden, where he spent practically the whole of the remainder of his life in work that has turned out to be of such importance to agricultural chemistry, most of which was given to the world in papers under the joint authorship of Sir John Lawes and himself.

In the year 1841 Sir Henry (then Dr.) Gilbert was elected a Fellow of the Chemical Society, within three months of its foundation. In 1882 and 1883 he held the office of President of the Society. In 1860 he was elected a Fellow of the Royal Society, and in 1867 he was awarded one of the Royal Medals.

Sir Henry Gilbert held several Professorships, and was a member of many agricultural and other learned societies, besides holding many honorary degrees.

MR. HENRY GEORGE MADAN.

WE have also to record with much regret the death of Mr. Henry George Madan, the Senior Fellow of Queen's College, Oxford, which occurred at Bearland House, Gloucester, on Sunday evening, the 22nd of December, 1901.

Mr. Madan was born on September 6th, 1838, and was therefore sixty-three years of age. He was educated at Marlborough College, whence he obtained an open exhibition at Corpus Christi College, Oxford, in 1857. He obtained a second-class at Classical Moderations in 1858, and a first-class in Natural Science in 1861.

In the year 1862 Mr. Madan was elected Fellow of Queen's College, and for some time acted as assistant to Sir Benjamin Brodie, the then Professor of Chemistry.

He was for twenty years the Head of the Science Department at Eton. Mr. Madan was a Fellow of the Chemical Society, and was the joint author with Mr. A. G. V. Harcourt, of Christchurch, of "Exercises in Practical Chemistry," and of several other smaller works on chemistry and physics. Some months ago Mr. Madan was knocked down by a railway truck in the docks at Gloucester, and suffered injuries which necessitated the amputation of his right arm, and affected his health in a manner which he never got over. His death will be regretted by a large circle of sympathetic friends.

CORRESPONDENCE.

NIOBIUM IN TUNGSTEN MINERALS AND METALS.

To the Editor of the Chemical News.

SIR,—Of the raw materials of steel-making tungsten compounds only are definitely known to sometimes contain niobium. An analysis by Bodenbender showed the presence of 1.22 per cent niobic oxide in wolframite, and the element is said to find its way into metallic tungsten powders.

Many who have to make analyses of these materials would be pleased to learn whether any reliable means of detecting and estimating small amounts of niobium are known. One's quest in this direction is somewhat complicated by the element being sometimes called niobium and sometimes columbium.

Osborne's paper "On the Quantitative Estimation of Niobium" (CHEMICAL NEWS, liii., 43) calls attention to the presence of small amounts of fluorides entirely preventing the hydrogen peroxide colour with titanium solutions, which is recalled by Hillebrand's warning against fluoriferous hydrogen peroxide (CHEMICAL NEWS, lxxxiv., 311; and lxxii., 158).—I am, &c.,

HARRY BREARLEY.

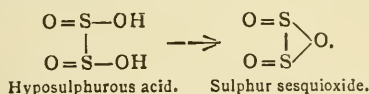
Bower Road, Sheffield.

THE CONSTITUTION OF SULPHUR SESQUIOXIDE.

To the Editor of the Chemical News.

SIR,—Sulphur sesquioxide is generally represented by the formula S_2O_3 ; I think the facts show that it should be formulated S_4O_6 .

Sulphur sesquioxide is by some looked upon as the anhydride of hyposulphurous acid,—



But such a view must be considered untenable, for, by hydrolysis, it neither yields hyposulphurous acid nor its products of decomposition.

It is also impossible to devise any satisfactory structural formula for S_2O_3 which will represent its formation from sulphur trioxide and sulphur, and its (easy) decomposition into sulphur dioxide and sulphur.

For the formula S_4O_6 , I put forward the following facts:—

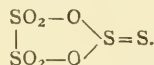
SO_2 is a gas,
 SO_3 is practically a liquid,
 S_2O_7 is hardly a solid,
and S_2O_3 is a crystalline solid.

The increase in melting-point cannot wholly depend upon the degree of oxidation, for then sulphur sesquioxide

would have the lowest melting-point. Neither can it wholly depend upon the degree of sulphonation, for then SO_2 , for instance, would have a higher melting-point than SO_3 . It might be urged that sulphur sesquioxide had a high melting-point because it had two atoms of sulphur; but, now, SO_3 has a higher melting-point than SO_2 , consequently the oxygen does to some extent increase the melting-point; and, upon the same reasoning, if sulphur sesquioxide were S_2O_3 , it should have a lower melting-point than S_2O_7 . In fact, the only way we can account for the higher melting-point of sulphur sesquioxide is by assigning to it the formula S_4O_6 ; it will then fall in its right position:—

SO_2 = 3 atoms.
 SO_3 = 4 "
 S_2O_7 = 9 "
 S_4O_6 = 10 "

As to its structural formula, the following may be put forward:—



This well represents its formation from sulphur trioxide and sulphur, and also the ease with which it decomposes into sulphur dioxide and sulphur. A little consideration will also show that it represents the products formed by the hydrolysis of sulphur sesquioxide (sulphuric, sulphurous, thiosulphuric, pentathionic acids, and sulphur), but space forbids the graphical representation which is necessary.—I am, &c.,

A. LIONEL LANDAU.

20, Highbury Park, N.,
December 23, 1901.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 24, December 9, 1901.

Researches on Radium.—H. Berthelot.—The author obtained a specimen of radium from M. Curie. He especially examined two interesting points; the part played by phosphorescence, and the order of greatness of the energies brought into action by the intervention of this new element. He operated at temperatures of 10° and 100° , always under atmospheric pressure, and varying the time of the action of radium. In each case three experiments were performed with iodic acid, one a blank, one in presence of a tube containing radium, and susceptible to the action of phosphorescence, and, finally, an experiment in presence of the same tube surrounded by black paper to intercept all influence which might be due to phosphorescence. An examination of the action produced was made at the end of definite periods of time.

Radio-activity of Uranium.—Henri Becquerel.—The radio-activity of uranium has been proved not to be constant. M. Giesel in particular showing that after certain treatments preparations of uranium became less active, and Sir W. Crookes, by fractional crystallisations, obtained inactive uranium nitrate. Reviewing these and various other researches on this subject, the author puts forward an hypothesis which apparently agrees with observed facts. If the emission of deviable rays identical with kathode rays were the cause of the emission of non-deviable radiation, which is so much like X rays, this spontaneous emission could be compared to the evaporation of an odorous body, the radio activity resembling a known phenomenon. The dissipated energy would be

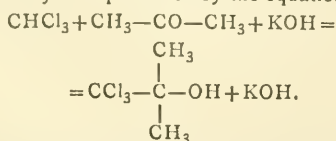
given out from the active body itself, but the corresponding loss of weight would be too feeble to be observed.

Alloys of Aluminium and Magnesium.—O. Boudouard.—A previous research on the fusibility of alloys of aluminium and magnesium enabled the existence of two definite compounds, AlMg_2 and AlMg , to be predicted. By utilising the known constants, by a microscopic examination, and also by chemical methods, the author was able to isolate, in addition to the others, the compound Al_4Mg . M. Le Chatelier's method was used, but the results were not very satisfactory in general. However, crystals of Al_4Mg were separated by attacking the metallic mixture with a 10 per cent solution of hydrochloric acid. By varying the proportions of aluminium from 0 to 100 per cent the author prepared a series of nine specimens which were examined under the microscope, the surfaces being attacked by suitable reagents.

Alloys of Strontium with Zinc and Cadmium.—Henri Gautier.—The author first repeats, with strontium chloride, the experiments described by Caron for the preparation of a zinc-calcium alloy from calcium chloride. Under these conditions an alloy of zinc and strontium is formed, but by varying the proportions of the materials employed and the temperature of the reaction, it was impossible to obtain an alloy containing more than 2 to 3 per cent of strontium. To facilitate the liberation of the strontium, and the formation of its alloy with zinc, he treated the strontium chloride with sodium in presence, not of zinc, but of zinc chloride. By this means an alloy containing 12 to 14 per cent of strontium was obtained. To prepare still richer alloys the strontium chloride was replaced by the iodide. Analogous experiments were then made by replacing the zinc by cadmium, a much more volatile metal. The alloys formed were enriched by distillation in a glass vessel at a very low pressure. An 18 to 20 per cent alloy of the alkaline earth metal after three hours' heating became a 28 per cent alloy, and after a whole day's heating a 45 per cent alloy was obtained.

Silicon in the Unstable Ferrosilicides.—P. Lebeau.—The different authors who have investigated the form under which silicon exists in cast iron and steel, have arrived at no definite opinion. The author's present researches on this subject lead him to conclude that the unstable ferrosilicides contain all their silicon in the combined state as SiFe_2 . This compound being very soluble in an excess of iron easily gives a homogeneous mass on cooling. This substance can only be obtained in the free state from the silicated products when it is present in a greater proportion than that which makes a saturated solution in the iron towards the solidification point. These results are in perfect agreement with M. Le Chatelier's experiments and the micrographic researches of M. Stead.

A New Practical Method of preparing Trichlorated Butylic Alcohol.—Marcel Guédras.—Trichlorated butylic alcohol can be rapidly prepared as follows:—Some caustic potash is placed in a little flask, and upon this, drop by drop with continual shaking, a mixture of chloroform and acetone in equal proportion is poured. During this operation the flask is heated to 30° . When the whole of the mixture has been introduced the flask is kept at a temperature of 50° for an hour. It is then heated to 60° , but must not reach 70° , in order to remove the excess of acetone and chloroform. There then remains in the flask trichlorobutyl alcohol and potash besides impurities. The reaction may be represented by the equation:—



The contents of the flask are treated with a current of steam, which removes the trichlorobutyl alcohol, and

which separates out on cooling in the form of white crystals. This alcohol possesses a very characteristic camphorated smell. It melts at $80-81^\circ$, and boils at 167° . It is almost insoluble in cold water, but dissolves to the extent of 2 per cent in hot water. It is soluble in ether, benzene, glacial acetic acid, strong alcohol, chloroform, and acetone. The dilute alkalis and acids have no action on it. Trichlorobutyl alcohol is a local anæsthetic, and also possesses antiseptic properties.

MISCELLANEOUS.

British Columbia Institute of Assayers.—At the meeting held at Nelson on November 8th, A. McKillop, chairman, it was unanimously resolved that an Association of the Assayers of British Columbia be forthwith inaugurated. The Constitution and By-laws, as drafted in Committee, were adopted in their entirety by unanimous vote. That this Association should prove of great advantage in many ways to assayers, and indeed to all interested in the Mining industry, is hardly to be doubted. Its value will depend, in a large degree, on the number of certified assayers being included in its membership.—J. CUTHBERT WELCH, Secretary *pro tem*. Office: Trail, B.C., December 13th, 1901.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Society of Chemical Industry, 8. "Report of the Joint Arsenic Committee of the Society of Chemical Industry and of the Society of Public Analysts." "The Retarding Influence of Aldehydes upon the Maturation of Spirits," by Prof. J. T. Hewitt, M.A., D.Sc., Ph.D.

TUESDAY, 7th. } Royal Institution, 3. (Christmas Lectures to Young
THURSDAY, 9th. } People). "On Waves and Ripples in Water, Air, and Ether," by Professor J. A. Fleming, M.A., F.R.S., D.Sc.

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"In this charming little book the reader is unconsciously introduced to problems which have previously defied solution."—*The Lancet*.

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ACETONE.

JOHS. OSWALDOWSKI,
ALTONA, near HAMBURG.

THE CHEMICAL NEWS.

Vol. LXXXV., No. 2198.

THE CONSTITUTION OF TOURMALINE.*

By F. W. CLARKE.

SOME years ago, in an extended paper upon the constitution of the silicates (*Bull. U.S. Geol. Survey*, 1895, No. 125), I proposed a formula for tourmaline which seemed to satisfy all known conditions. Recently, Penfield and Foote (*Amer. Journ. Sci.*, 1899, Fourth Series, vol. vii., p. 97) have offered still another interpretation of the analyses, and support their views with a considerable weight of argument. The appearance of their paper has led me to re-scrutinise the evidence more in detail than previously, and the result has been to modify my formulæ in some particulars while retaining them in their general form.

According to Penfield and Foote all tourmaline may be represented as salts of the aluminoborosilicic acid, $H_{11}Al_3B_3Si_4O_{21}$, in which two hydroxyls are permanently linked to boron, leaving an available valency or basicity of nine. In my formulæ all tourmalines are derived from the similar acid $H_{14}Al_5B_3Si_6O_{31}$, with all of the hydrogen atoms replaceable by bases. Upon bringing the two acids to the common basis of six silicon atoms, they compare as follows:—

Penfield and Foote $H_{16.5}Al_{4.5}B_3Si_6O_{31.5}$
Clarke $H_{14}Al_5B_3Si_6O_{31}$

Replacing aluminum by hydrogen in order to show the ultimate acids these expressions become:—

Penfield and Foote $H_{30}B_3Si_6O_{31.5}$
Clarke $H_{29}B_3Si_6O_{31}$

The small difference between the empirical formulæ is thus made evident, and it hardly amounts to more than the uncertainties in the analyses. In fact, the trustworthy analyses of tourmaline give ratios lying between and beyond both extremes, as the following formulæ, computed from Riggs's data, show. In these expressions fluorine has been assumed equivalent to hydroxyl:—

Pierrepont, black $H_{28.87}B_{2.93}Si_6O_{30.83}$
Paris, black $H_{30.73}B_{2.66}Si_6O_{31.35}$
Stony Point, black $H_{30.23}B_{3.02}Si_6O_{31.65}$
Auburn, colourless $H_{29.25}B_{2.77}Si_6O_{30.78}$
Brazil, red $H_{30.79}B_{2.78}Si_6O_{31.56}$
Gouverneur, brown $H_{28.36}B_{2.95}Si_6O_{30.61}$
Hamburg, brown $H_{30.93}B_{3.05}Si_6O_{32.14}$

The two analyses by Penfield and Foote, however, conform sharply to their formula, thus:—

De Kalb, white $H_{29.85}B_{3.03}Si_6O_{31.48}$
Haddam Neck, green $H_{29.98}B_{3.06}Si_6O_{31.59}$

The Gouverneur and Hamburg tourmalines represent the extreme range of variation; a variation which is too large to be safely set aside as due to analytical errors or to impurities in the material analysed. Some of the formulæ approximate to mine, some to that of Penfield and Foote, and hence it seems probable that neither formula, without some qualification, can safely be taken as final.

In order to be satisfactory, a constitutional formula must fulfil several conditions. First, it must adequately express the composition of the compound in question, covering all of its variations. Second, it must be readily applicable to the full discussion of analyses, so that the different isomorphous salts which are commingled in a

mineral species can be separately identified and given reasonable expressions. Finally, it should indicate the relations between a species and the other minerals with which it is allied, or into which it commonly alters. A formula can be fully adopted only when all of these conditions are satisfied. The third condition, which relates to function, is equally important with the other two.

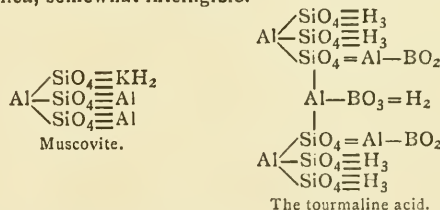
With the tourmalines, the micas seem to be most nearly akin. In each group we have to consider comminglings of isomorphous molecules, and when tourmaline alters, a mica is commonly the product of the reaction. In composition, also, the two groups show an apparent parallelism. With the lithia mica, lepidolite, lithia tourmalines occur; with muscovite and biotite, the common iron tourmaline is associated; and the magnesian tourmalines, which show the minimum of alumina in their composition, are similarly allied to phlogopite. This relationship, if it is real, should be suggested in the formulæ assigned to the several species.

To the commoner micas a simple series of formulæ can be easily given thus:—

Muscovite $Al_3(SiO_4)_3KH_2$,
Biotite $Al_2(SiO_4)_3Mg_2KH$,
Phlogopite $Al_1(SiO_4)_3Mg_3KH_2$;

and to these types, or mixtures of them, most micas are referable. The variations and exceptions have been considered elsewhere, and need not be discussed here.

With these fundamental molecules the corresponding salts of the tourmaline acid, $H_{29}B_3Si_6O_{31}$, or $H_{14}Al_5B_3Si_6O_{31}$, are structurally correlated. The subjoined formulæ are sufficient to make this point clear; and to render the splitting up of tourmaline, its alteration into mica, somewhat intelligible.



In the acid, two hydrogen atoms are united with the orthoboric group, and twelve with the orthosilicate portion of the nucleus. Hence, to avoid repetition of the structural expression, the formula may be condensed into a linear form as follows:— $Al_5(SiO_4)_6(BO_2)_2.BO_3H_2.H_{12}$, and this is applicable to the discussion of the analyses. For example, Riggs's analysis of the black magnesium tourmaline from Pierrepont, New York, corresponds to the following molecular mixture:—

13. $Al_5(SiO_4)_6(BO_2)_2.BO_3Ca.Mg_4H_4$
7. $Al_5(SiO_4)_6(BO_2)_2.BO_3Mg.Mg_4H_4$
2. $Al_5(SiO_4)_6(BO_2)_2.BO_3Na_2.Al_2Na_4H_2$

Comparing this with the analysis, and reducing the latter by union of like bases and re-calculation to 100 per cent, we have:—

	Found.	Reduced.	Calculated.
SiO ₂	35'61	37'19	37'05
B ₂ O ₃	10'15	10'51	10'80
Al ₂ O ₃	25'29	27'10	27'19
Fe ₂ O ₃	0'44		
TiO ₂	0'55		
CaO	3'31	3'45	3'40
FeO	8'19	16'31	16'28
MgO	11'07		
Na ₂ O	1'51	1'72	1'74
K ₂ O	0'20		
H ₂ O	3'34	3'72	3'54
F	0'27		
	99'93	100'00	100'00

* Bulletin of the United States Geological Survey, No. 167.

The result is evidently satisfactory. In dealing with titanium I have followed Penfield, regarding it as really Ti_2O_3 , and equivalent to alumina. The fluorine is treated as replacing hydroxyl, and is therefore united with the water. It is possible, however, that fluorine may sometimes replace the group BO_2 , an equivalency which is strongly indicated in the cappelinite group of minerals.

The brown tourmaline from Gouverneur, New York, as analysed by Riggs, also reduces to a similar mixture of molecules, and its composition may be written thus:—

5. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Ca}.\text{Mg}_4\text{H}_4$,
3. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Mg}.\text{Mg}_4\text{H}_4$,
2. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{NaH}.\text{Al}_2\text{Na}_2\text{H}_4$;

and the comparison between analysis and theory is as follows:—

	Found.	Reduced.	Calculated.
SiO_2	37.39	37.54	37.32
B_2O_3	10.73	10.76	10.88
Al_2O_3	27.79		
Fe_2O_3	0.10	28.72	28.53
TiO_2	1.19		
FeO	0.64		
MgO	14.09	14.51	14.52
CaO	2.78	2.79	2.90
Na_2O	1.72	1.83	1.93
K_2O	0.16		
H_2O	3.83	3.85	3.92
	100.42	100.00	100.00

By consolidating lime with magnesia the expressions for both tourmalines might be simplified; but in other cases this would not be warranted. In some tourmalines calcium seems rather to replace sodium, or else the group NaH , a probability which will appear later.

In these two tourmalines the theoretical silicon-oxygen ratio Si_6O_{31} is assumed, in accordance with my original formula. We may now consider the cases in which that ratio is exceeded, with more or less approach to the formula proposed by Penfield and Foote. This condition is easily satisfied by regarding one of the component salts of tourmaline as slightly basic, containing the bivalent group $=\text{Al}-\text{O}-\text{H}$ or $=\text{Al}-\text{F}$ as an essential factor. With this assumption, which recognises the equivalency of hydroxyl and fluorine, the analyses reduce to the general type indicated in the two preceding examples. For instance, the white tourmaline from De Kalb, New York, has the following composition:—

10. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3(\text{AlOH}).\text{Mg}_4\text{H}_4$.
20. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Ca}.\text{Mg}_4\text{H}_4$.
3. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Na}_2.\text{Al}_3\text{Na}_3$.

For comparison the analyses by Penfield and Foote and by Riggs are available. In this case the minute quantities of titanium are ignored.

	Found.		Reduced.		Mean.	Calculated.
	P. and F.	Riggs.	P. and F.	Riggs.		
SiO_2 ..	36.72	36.88	36.56	36.81	36.69	36.79
TiO_2 ..	0.05	0.12	—	—	—	—
B_2O_3 ..	10.81	10.58	10.76	10.56	10.66	10.74
Al_2O_3 ..	29.68	28.87	29.55	28.81	29.18	29.07
FeO ..	0.22	0.52	14.97	14.79	14.88	14.86
MgO ..	14.92	14.53				
CaO ..	3.49	3.70	3.47	3.69	3.58	3.48
Na_2O ..	1.26	1.39	1.28	1.50	1.39	1.44
K_2O ..	0.05	0.18				
H_2O ..	2.98	3.56				
F ..	0.93	0.50	3.41	3.84	3.62	3.62
	101.11	100.83	100.00	100.00	100.00	100.00

The dark brown tourmalines from Orford, New Hampshire, and Monroe, Connecticut, as analysed by Riggs, also reduced to similar form, and approximate to the mixture—

15. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3(\text{AlOH}).\text{Mg}_4\text{H}_4$,
6. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Ca}.\text{Mg}_4\text{H}_4$,
8. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{NaH}.\text{Al}_3\text{Na}_2\text{H}_4$,

with the comparison as follows:—

	Found.		Reduced.		Calculated
	Orford.	Monroe.	Orford.	Monroe.	
SiO_2 ..	36.66	36.41	36.96	37.34	36.84
B_2O_3 ..	10.07	9.65	10.16	9.89	10.74
Al_2O_3 ..	32.84	31.27			
TiO_2 ..	0.23	1.61	33.28	33.13	33.11
FeO ..	2.50	3.80			
MgO ..	10.35	9.47	11.84	11.88	11.85
CaO ..	1.35	0.98	1.36	1.00	1.19
Na_2O ..	2.42	2.63	2.58	2.88	2.62
K_2O ..	0.22	0.21			
H_2O ..	3.78	3.79	3.82	3.88	3.65
	100.42	99.87	100.00	100.00	100.00

Here the divergence between the composition as found and as calculated is evidently due to the low determinations of boric acid in the analysis. Still the comparison is close.

(To be continued).

THE REACTION BETWEEN CHLORINE AND AMMONIA.*

By WILLIAM A. NOYES and ALBERT C. LYON.

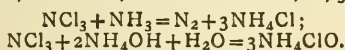
IN Hoffmann's well-known lecture experiment for the demonstration of the composition of ammonia, the introduction of the ammonia into the tube filled with chlorine is followed by the addition of dilute sulphuric acid. Some years ago, when performing this experiment, it occurred to one of us that the use of the sulphuric acid was unnecessary, as any excess of ammonia would be absorbed by the large amount of water which is allowed to enter the tube later. The sulphuric acid was accordingly omitted, but with the surprising result that the tube was left only one-sixth full of nitrogen instead of one-third full, as it should have been. Recently an opportunity has been found to give the subject a more careful study.

A glass tube, having a capacity of about 95 c.c., and closed at each end with a stop-cock, was prepared. This tube, after cleaning and drying, was filled with chlorine which was generated from manganese dioxide and hydrochloric acid, and washed with water. The gas was passed through the tube from below till the portion escaping was completely absorbed by a solution of sodium hydroxide. After removing the chlorine from the tubes outside of the stop-cocks, aqua ammonia was allowed to enter the tube from above, and, after shaking gently, was followed by water till the residual gas was at atmospheric pressure. The amount of the nitrogen was then determined by filling the tube with water from a burette which was connected with its lower end.

It was soon found that when strong ammonia is used in excess the volume of the nitrogen is considerably greater than one-sixth of the volume of the chlorine, and may approach one-third of the volume of the chlorine, but never reaches that limit. If, however, a solution containing 0.5 per cent of ammonia is used in such amount as to leave the solution faintly acid, the volume of the nitrogen approaches very closely to one-sixth the volume of the chlorine. If a 2 per cent solution of ammonium chloride is used instead of the ammonia, the chlorine is almost completely absorbed, and the volume of the nitrogen may

* The work described in this paper forms the subject of a thesis by Mr. Lyon for the degree of Bachelor of Science at the Rose Polytechnic Institute. From the *Journal of the American Chemical Society*, xliii., No. 7.

be as low as only 1 or 2 per cent of the volume of the chlorine. As will be shown below by quantitative results, the normal reaction between chlorine and ammonia is $2\text{NH}_3 + 3\text{Cl}_2 = \text{N}_2 + \text{NCl}_3 + 6\text{HCl}$. This normal reaction is obtained, however, only when the ammonia is used very nearly in the proportion indicated. If an excess of ammonia is used, it reacts in part with the nitrogen trichloride, giving free nitrogen, in part, probably, giving ammonium hypochlorite (Schönbein, *Journ. Prakt. Chem.*, lxxxiv., 386; Fresenius, *Zeit. Anal. Chem.*, ii., 59).



If, on the other hand, too little ammonia is used, the ammonium chloride formed by the reaction acts, in part, on the chlorine as stated above, with little or no evolution of nitrogen, and the volume of nitrogen liberated will be less than one-sixth the volume of the chlorine.

In studying the reaction quantitatively, the tube described above was covered with dark paper to prevent the action of light on the nitrogen trichloride formed. After filling the tube with chlorine an amount of 0.5 per cent ammonia solution, equal to from 90 to 95 per cent of that required by the reaction, was allowed to enter, the tube was shaken gently, and then water of the temperature of the original gas allowed to enter to atmospheric pressure. After gentle shaking a small additional amount of water would enter, indicating that an absorption of some kind had taken place, and the shaking was repeated till no more water would enter. Whether this small final absorption is due to residual chlorine, or to the fact that nitrogen trichloride has an appreciable vapour-pressure, and is not quickly absorbed by the water, was not determined. The lower end of the tube was then connected with a burette and the amount of water required to fill the tube gave the volume of the residual nitrogen.

The contents of the tube were then transferred to a separatory funnel containing 10 c.c. of benzene (Hentschel, *Ber. d. Chem. Ges.*, xxx., 1434), shaken, the benzene separated, and this repeated twice more. The benzene containing the nitrogen trichloride was shaken at once with an excess of a solution of arsenious oxide in sodium bicarbonate, and the excess of arsenious oxide determined with a standard iodine solution. The reaction is $3\text{As}_2\text{O}_3 + 2\text{NCl}_3 + 15\text{H}_2\text{O} = 2\text{NH}_4\text{Cl} + 4\text{HCl} + 6\text{H}_3\text{AsO}_4$.

Each atom of chlorine present is therefore equivalent to 2 atoms of "available chlorine" (Hentschel, *loc. cit.*).

After titration the solution was distilled with an excess of caustic soda, and the ammonia in the distillate was determined by means of a standard acid, thus proving that the substance extracted by the benzene was really nitrogen trichloride.

The solution which had been extracted with benzene, and which was, as has been explained, still slightly acid, was titrated with the same ammonia solution first used, and the total ammonia required determined.

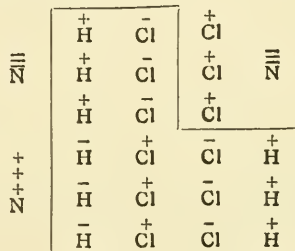
The results are as follows:—

	Calculated.	Found.				
		I.	II.	III.	IV.	V.
Volume of nitrogen as compared with chlorine	16.67	14.32	16.31	17.62	17.20	17.05
Available chlorine . 50.0		49.3	43.4	35.7	45.5	41.7
Molecules of ammonia per atom of chlorine	1.0	0.97	1.03	1.04	1.01	0.98
Ammonia from NCl_3 . Mols. per mol. of NCl_3 ..	1.0	0.95	1.10	1.10	1.14	—

Owing to the instability of the nitrogen trichloride and to the secondary reactions which can never be entirely avoided, an exact agreement cannot be expected. The results satisfactorily demonstrate that the reaction already given is the primary one between ammonia and chlorine.

Probably the most interesting feature of the reaction

here studied is the fact that 6 molecules of chlorine must react *simultaneously* with 3 molecules of ammonia, for, if the liberation of nitrogen by the action of 1 part of the chlorine were independent of the formation of nitrogen trichloride by another part, the constant relation of 1 volume of nitrogen to 6 volumes of chlorine would be improbable. The following hypothesis as to the cause of this relationship is given with some hesitation and in the hope that it may lead to discussion, and to a further consideration of similar cases. If we suppose, what seems not inherently improbable, that all reactions involving the decomposition of molecules are preceded by an ionisation of the parts of those molecules, it would follow that elementary molecules, as well, may ionise into positive and negative parts. This explanation of the reaction may be represented graphically thus:—



The explanation given involves the further idea that in the ionisation of ammonia the hydrogen may become either positive or negative. When we remember the neutral character of ammonia, and the fact that its hydrogen may be replaced by either chlorine or sodium, such a thought is not so improbable as it seems when first presented.

That the hypothesis here suggested is capable of a wide application need hardly be said.

A RAPID METHOD FOR THE DETERMINATION OF ARSENIOS OXIDE IN PARIS GREEN.

By S. AVERY and H. T. BEANS.

THE authors have been working for some time on a method for determining the arsenic in Paris green, in the hope that one might be found that would be both more rapid and accurate than any thus far proposed. As a result we offer the following method, which we believe to be new and which has given most excellent results on a considerable number of samples of Paris green examined in this laboratory.

For the determination, sample the Paris green by quartering (as one would an ore for assaying) down to about 1 gm. Pulverise this small sample in an agate mortar and weigh out 0.2 to 0.3 gm. into a beaker of about 300 c.c. capacity. Add about 25 c.c. of water and to the green suspended in water add, with constant stirring, concentrated hydrochloric acid till solution is just effected; from 6 to 10 drops are usually sufficient. Now add to the acid solution sodium carbonate solution till a slight permanent precipitate is formed, and at this point add 2 to 3 grms. of sodium potassium tartrate in solution. The tartrate will at once dissolve the precipitated copper and prevent further precipitation during the subsequent titration. Dilute to about 200 c.c., add solid sodium bicarbonate and starch solution, and titrate with iodine in the usual way.

The time required for the determination is about ten minutes. The end reaction is sharp and is not in the least obscured by the blue colour of the copper solution.

Triplicate determinations on the same sample of a very

uniform Paris green were as follows, taking 0.3 gm. Paris green for analysis.

Iodine solution c.c.	As ₂ O ₃ Grm.	As ₂ O ₃ Per cent.
34'52	0'17056	56'85
34'59	0'17091	56'97
34'58	0'17086	56'95

To make sure that the presence of copper exerted no influence, several lots of pure arsenious oxide were weighed out. Some of these were titrated as usual and the others were first mixed with about an equal weight of copper sulphate in solution and then with the tartrate according to the method given. No appreciable difference could be observed in the several titrations.

Several other analysts, as well as ourselves, have found that the results, in terms of metallic arsenic, obtained by this method are slightly higher than the results by other methods, even when the latter admit of the determination of arsenic in either stage of oxidation. This fact would seem to indicate that the Paris greens on the market contain arsenic in the lower stage of oxidation only.

Cuprous oxide interferes with the titration, but we have not observed the presence of copper, in this degree of oxidation, in any of the samples examined. It is, of course, possible that adulterants might be added that would affect iodine or iodine salts, but such samples have not as yet been met with, to our knowledge.

In conclusion, we would express our obligations to Dr. H. W. Wiley for his kindness in having the literature of the subject thoroughly searched for our guidance.—*Journal of the American Chemical Society*, xxiii., No. 7.

MODIFIED WILLIAMS METHOD FOR MANGANESE.

By RANDOLPH BOLLING.

THE Williams method, as outlined in Blair's "Chemical Analysis of Iron," although a very accurate one, is unsatisfactory on account of the time required for the filtration of the precipitated manganese dioxide, which, together with a frequently occurring mass of gelatinous silica, chokes up the asbestos filter, and makes the operation more or less tedious.

The following modification has been found to overcome this difficulty entirely, and its adoption has reduced the time of a determination very materially, by eliminating the uncertainty attendant upon the filtration of the slimy manganese dioxide.

Method.

Place 5 grms. of pig-iron drillings in a No. 5 Griffin's beaker, with cover glass, add 75 c.c. nitric acid (sp. gr. 1'20), and after violent action has ceased add approximately 10 c.c. hydrofluoric acid. Give the beaker a circular motion to mix contents, and evaporate down until ferric oxide begins to separate out. Cool, add 100 c.c. nitric acid (sp. gr. 1'42), and heat to boiling. Drop in a spoonful of asbestos fibres, and then add approximately 7 grms. potassium chlorate. Boil until green fumes disappear and nitric acid begins to volatilise. Remove from source of heat, cool rapidly, and filter the manganese dioxide precipitated on the suspended asbestos fibres, on a special filtering tube. Wash twice with strong nitric acid, and rinse out the beaker in which the precipitation was made with cold water, pouring the rinsings through the filter-tube. Continue the rinsing and washing until, when tested with litmus, no acidity is shown. Push the asbestos pad, and precipitate back into the beaker, wash down the sides of the filter-tube to remove all adherent manganese dioxide, and run in 50 c.c. acid ferrous sulphate solution. Disintegrate the asbestos fibres with a stirring rod, and after the precipitate is

entirely dissolved, titrate with permanganate. The filtering-tube is prepared by taking a glass tube thin enough to slide loosely down the stem of a carbon funnel, heating one end until it balls, and then pressing out flat. By softening the edge of the flat end, and pressing a nail against the circumference at regular intervals the disk can be made fluted. Slip this rod in a carbon funnel, pushing down until the disk rests solidly, place on it a little dry asbestos, and then pour on it asbestos suspended in water, using a moderate suction to make the pad fairly compact.

Acid Ferrous Sulphate.

Dissolve 20 grms. chemically pure ferrous sulphate in water, add 200 c.c. strong sulphuric acid, and dilute to 2 litres.

Potassium Permanganate Solution.

The strength of this solution should be such that 1 c.c. equals about 0.0056 gm. iron.

Standardisation and Calculation of Results.

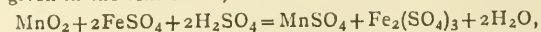
To standardise both the ferrous sulphate and the permanganate at the same time, take an iron in which the manganese has been accurately determined, and treat it according to the method given until the precipitate of manganese dioxide is obtained. Dissolve the precipitate in 50 c.c. of ferrous sulphate solution, and titrate with permanganate, then run in 50 c.c. additional of the ferrous sulphate, and titrate again, to obtain the amount of permanganate necessary to oxidise 50 c.c. of the ferrous sulphate solution. By deducting the number of cubic centimetres used in the first titration from the number used in the second, we obtain the volume of solution oxidised by the manganese dioxide. Dividing the percentage of manganese in the sample by the figure thus obtained, and multiplying this by the number of grms. of the original sample, we obtain the value of 1 c.c. permanganate in terms of manganese. For instance, if we take 5 grms. of a pig-iron containing 1.13 per cent manganese and use 4.6 c.c. permanganate in the first titration and 20.8 c.c. in the second titration, then the difference of 16.2 c.c. is the measure of the amount of ferrous sulphate oxidised by the manganese dioxide. Dividing 1.13 by this 16.2, and multiplying this by 5, we obtain the value of 1 c.c., or 0.0034 gm. manganese. The object of standardising in this way, is to carry out the process under conditions similar to those which occur in a regular determination, for the results obtained by titrating clear ferrous sulphate are always lower than when carbon and asbestos are in the solution, for the reason that the eye of the observer notices the rose tint at once in a transparent solution, but the sharpness of the end reaction is slightly obscured by asbestos and carbon, hence the operator runs a little past the true point. So that if both titrations are made under like conditions this error is completely eliminated.

The calculations in a determination are made thus:—If 5 grms. of the sample are taken, 50 c.c. ferrous sulphate equals 20.8 c.c. permanganate; 1 c.c. permanganate equals 0.0034 manganese; 6.2 c.c. are required to oxidise the ferrous sulphate not oxidised by the manganese dioxide.

Then

$$\frac{(20.8 - 6.2) \times 0.0034 \times 100}{5} = \text{per cent manganese.}$$

The time saved by the suspension of the manganese dioxide, and the elimination of silica in the filtering of the manganese dioxide, makes it possible to make a determination in about one hour. The method of standardising solutions is not based on the reaction that is given in the text-books, which is—



as it was found that solutions standardised on the above reaction were invariably too low in their manganese value. This may be accounted for in the composition of

the precipitate, for it is possible that MnO , Mn_2O_3 , Mn_3O_4 , Mn_5O_7 , may be formed in part. At any rate, if we adopt the MnO_2 theory and standardise accordingly, the method will not give the same result as a sample that has the manganese determined by the basic acetate separation, and the manganese weighed as manganese pyrophosphate according to Gibbs. On this account it is preferable to use a standardised sample of pig-iron.

Below are given some determinations on ores and on some very carefully standardised pig-iron.

Results in the first column are by using the Gibbs method.

In the second column by modified Williams method.

In the third by old Williams method, using the MnO_2 theory.

		Sample No.	Percentage of manganese.		
Iron ores	1.	1.38	1.39	1.11	
	2.	1.84	1.84	1.51	
	3.	1.08	1.06	0.91	
	4.	1.34	1.35	1.20	
	5.	0.10	0.12	0.08	
	6.	2.87	2.87	2.14	
	7.	2.07	2.07	1.83	
Pig-iron	8.	0.415	0.41	0.37	
	9.	0.442	0.44	0.38	
	10.	0.97	0.99	0.81	

In working on ores carrying large amounts of silica it is advisable to dissolve the sample in hydrochloric acid, and evaporate down to dryness, then moisten with hydrochloric acid, and heat until the mass softens, and then add a few cubic centimetres of strong nitric acid; evaporate again until chlorine is driven out, and then add hot water, and filter off the silica, and evaporate filtrate and determine manganese as usual.

I wish to acknowledge my thanks to Mr. W. Walley Davis, chief chemist, for his suggestions in regard to arranging the analytical data for publication.—*Journal of the American Chemical Society*, xxiii., No. 7.

NOTES ON THE ANALYSIS OF EXPLOSIVES.

By F. W. SMITH.

Determination of Sulphur.

In gelatin dynamite containing from 1 to 3 per cent of sulphur, the following method is useful:—Weigh out about 2 grms. into a silver crucible of 100 c.c. capacity; fill it two-thirds full with an alcoholic solution of caustic soda. Warm carefully on a water-bath until the nitroglycerin is decomposed and then evaporate to dryness. Add next about 40 grms. of solid caustic potash and 5 grms. of potassium nitrate. Fuse the contents of the crucible carefully over a blast-lamp until all organic matter is oxidised. Dissolve in dilute acetic acid, filter from a small amount of insoluble matter, and precipitate the sulphates with the usual precautions. The results check very closely.

An Indirect Method for the Estimation of Nitroglycerin in Gelatin Dynamite, &c.

About 15 grms. of the sample are completely extracted with chloroform in a Soxhlet apparatus and the loss in weight noted. In another portion the moisture is determined by desiccation over sulphuric acid for five days, careful experiments having shown that nitroglycerin is not appreciably volatile in a desiccator. Another portion of about 2 grms. is carefully extracted with pure ether by maceration in a small beaker. The ether is poured through a filter and the extraction repeated three or four times. The filtrate is now allowed to evaporate spontaneously or with the aid of a gentle current of air. When the ether is evaporated add about 5 c.c. of ammonium sulphide

solution and 10 c.c. of alcohol. Warm gently on a water-bath until the nitroglycerin is decomposed, and then add about 250 c.c. of water and enough hydrochloric acid to give a strongly acid reaction, filter, and wash the precipitate free from acid. Now wash the precipitate out with strong alcohol and chloroform, collecting this filtrate in a weighed platinum dish. Evaporate at a low temperature and dry to constant weight at 50° C. The contents of the dish are now transferred to a silver crucible and the sulphur determined as above described. The increase in weight of the dish less this amount of sulphur represents the chloroform-soluble substances in the original sample except the nitroglycerin, moisture, and sulphur. The percentage of the former substances plus the moisture and sulphur in the original sample gives, when subtracted from the total chloroform-soluble, the percentage of nitroglycerin.

In another portion, the residue in the platinum dish may be investigated for resins, paraffin, &c.

On the Use of Lunge's Nitrometer.

All the glass stop-cocks should be tight. In reference to the practical testing of stop-cocks, see *Journ. Am. Chem. Soc.*, xxi., 430.

Standardising the Nitrometer.—There are two methods applicable, the first of which I shall call "the absolute method," and the second the "empirical method." The latter was devised by Dr. Clarence Quinan, of San Francisco.

The first consists in admitting to the reduction tube a quantity of air such that if reduced to 0° C. and 760 m.m. pressure, it would occupy a volume of 100 c.c. The analysis is then made by weighing out a convenient quantity of nitrate, decomposing it in the usual way, introducing the nitric oxide into the measuring tube, and regulating the pressure so as to bring the volume of air in the reduction tube to 100 c.c., while the surface of the mercury in the measuring tube is at the same level as the surface of the mercury in the reduction tube. If deemed preferable the level of the mercury in the measuring tube may be made to coincide with the level of the mercury in the reservoir tube, so as to make the pressure in the measuring tube equal to the atmospheric pressure. The volume of nitric oxide is then read off and reduced to normal conditions by the usual calculations.

The correctness of the results obtained in this method, aside from errors of manipulation, is affected by the following factors:—

- The accuracy of the barometer.
- The accuracy of the thermometer.
- The accuracy of the graduation of the reduction tube.
- The accuracy of the graduation of the measuring tube.
- The accuracy of the weights employed.

It is evident that the work of calibrating all the instruments employed would be very considerable, and it is not safe to assume the correctness of such instruments as they occur in trade.

The empirical method is as follows:—

A sample of potassium nitrate is purified until it shows the absence of impurities by the ordinary tests. It is then dried and the nitric oxide derived from a known quantity is passed into a measuring tube. The quantity of air in the reduction tube is then varied until the volume of the nitric oxide is approximately that calculated from the amount of nitrate taken. The reduction tube is now sealed and a series of analyses of potassium nitrate made with slight variations in the amount taken, and in each case a correction factor determined which shows 100 per cent in purity in the nitrate taken (see example below). The extreme variations in the determinations should not exceed 0.05 per cent. From this series of determinations a correction factor is calculated which is applied to all determinations.

Example.

0.5078 grm. KNO_3 gave 111.7 c.c. nitric oxide.
 Log. 111.7 0.04805
 Log. 0.5078 0.70569

Log. of c.c. per grm. .. . 0.34236

0.5057 grm. KNO_3 gave 111.2 c.c. nitric oxide.
 Log. c.c. 0.04610
 Log. s. 0.70389

0.34221

0.5058 grm. KNO_3 gave 111.2 c.c. nitric oxide.
 Log. c.c. 0.04610
 Log. s. 0.70398

0.34212

The average of these logarithms gives: Log c.c. per grm. 0.34223 corresponding to 219.9. The correction is obtained by the proportion 221.0 : 219.9, the first term being the theoretical c.c. per grm. for potassium nitrate.

Log. 221.0 0.34428

Log. 219.9 0.34223

0.00205

In other words, in any analysis the mass of the logarithm representing the c.c. per grm. or the percentage of nitrogen must be increased by 0.00205.

Example.

0.5913 grm. gun-cotton gave 119.1 c.c. of nitric oxide.

Log. c.c. 0.07591

Log. s. 0.77181

0.30410

0.00205

0.30615

This corresponds to 202.3 c.c. per grm. or 12.71 per cent nitrogen.

The advantage of this method lies in the fact that all the sources of constant errors A to E are eliminated, no thermometer nor barometer being needed. The weights may be inexact if only consistent. The graduation of the tubes may be inexact and inconsistent. In fact they could be grossly inaccurate without affecting the accuracy of the results if separate corrections were made for each point on the measuring tubes.

The obvious objection to the method lies in the difficulty of preparing a pure potassium nitrate which shall not have a low content of nitrogen by reason of the presence of foreign matter, nor a high content of nitrogen from the presence of sodium nitrate. These objections may be met by preparing samples of potassium nitrate from different sources. All should show the same percentage of nitrogen. Secondly, a sample of nitrate of soda should be purified and the correction factor determined from it independently. Within the limits of experimental error it should be the same as the correction factor derived from potassium nitrate.

Example.

0.4302 grm. sodium nitrate gave 112.5 c.c. nitric oxide.

Log. c.c. 0.05115

Log. s. 0.63367

0.41748

Log. theoretical c.c. per grm.

for sodium nitrate .. . 0.41954

0.00206

As a third check a sample of pure dry nitroglycerin may be used.

At one time in my work the reduction tube was set by aid of a barometer, since shown to be faulty. A sample

of potassium nitrate carefully purified showed in this case about 99 per cent purity, and a sample of sodium nitrate also carefully purified showed the same percentage of purity within the limits of error. The barometer setting of the reduction tube was therefore discarded and the correction factor introduced, since it was manifest that, while either of the nitrates might be impure even after the most careful purification, it was in high degree improbable that both should be impure and of exactly the same degree of impurity.

During the hot weather of summer there is a distinct advantage in having a large subtractive correction factor. In this way the gas may be measured nearly at the pressure of the atmosphere, thus avoiding the considerable strain on the stop-cock and consequent tendency to leakage.

The nitric oxide may be measured either dry or moist, more conveniently, however, in the latter condition. If so measured, a few drops of water should be left in each tube. As the tension of the aqueous vapour is the same in each tube, it may be neglected in the calculations.

The sulphuric acid used in nitrometer work should be free from oxides of nitrogen and iron. It should be of 94 to 95 per cent strength. In acid of 98 per cent strength nitric oxide is quite freely soluble., *Journal of the American Chemical Society*, xxiii., No. 8.

THE VOLUMETRIC DETERMINATION OF ZINC.

By PERCY H. WALKER.

THE most commonly used method for the determination of zinc is the volumetric process of titrating with standard potassium ferrocyanide, using either a uranium solution or one of cobalt nitrate or platinum chloride as indicator. The ferrocyanide titration has several disadvantages. The standard solution does not keep well, and hence must be frequently standardised. If too much ferrocyanide is added in titrating, there is nothing to do but make another determination. The method of using an indicator, by taking out drops, invariably introduces an error.

R. K. Meade (*Journ. Amer. Chem. Soc.*, 1900, xxii., 353) has given us a method based on an entirely different reaction. He precipitates the zinc as zinc ammonium arsenate, and uses this arsenate to liberate iodine, which is then titrated by thiosulphate.

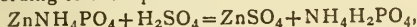
The most satisfactory gravimetric process for determining zinc is the precipitation of zinc ammonium phosphate, and weighing as pyrophosphate, an analogous process being applied to manganese and magnesium.

Many years ago, Stolba (*Chem. Centralbl.* 1866, 727, 728; Sutton's "Volumetric Analysis," Sixth Edition, p. 87) worked out an alkalimetric method for the determination of magnesium, by titrating the magnesium ammonium phosphate with standard acid. Handy's method (*Journ. Amer. Chem. Soc.*, 1900, xxii., 31) is a modification of Stolba's. This process may be much more easily used for the determination of zinc than for magnesium.

The process is carried out as follows:—To the zinc solution, which should also contain ammonium chloride, a large excess of ammonia is added, then a large excess of sodium phosphate. The solution remains clear; but if the excess of ammonia is cautiously neutralised, a white cloud is formed as each drop of acid falls into the strong ammoniacal liquid. On stirring this cloud dissolves until nearly all the ammonia is neutralised, when the whole solution becomes milky. It should now be heated to about 75° C., and stirred constantly, at the same time continuing the addition of dilute acid, drop by drop. In a very few minutes the precipitate becomes crystalline, and with care the liquid may be almost perfectly neutralised. It is a good plan to add a small piece of litmus-paper to the liquid; this should not turn red, but

should remain blue or violet, while the hot liquid should have no odour, or only a very faint odour of ammonia. When the precipitation is made as above, the zinc ammonium phosphate is easily filtered, which may be safely done after five minutes' standing. The precipitate should be washed with cold water until the washings show only a faint trace of chlorides, then the paper with the precipitate returned to the beaker in which the precipitation was made, an excess of standard acid added, a few drops of methyl orange, and the exact point of neutrality determined with standard alkali.

According to the equation—



we see that 1 c.c. of normal acid corresponds to 32.7 m.g. zinc. A solution of pure zinc oxide in hydrochloric acid was prepared for testing this method, the following results being obtained:—

	Zinc taken. Grm.	Zinc found. Grm.
1	0.1490	0.1486
2	0.1490	0.1481
3	0.1490	0.1486

Since the zinc ammonium phosphate is not precipitated in presence of a large excess of ammonia, the process may be used in the presence of magnesium which is precipitated in the strongly alkaline liquid, and the filtrate from the precipitate neutralised to precipitate the zinc. About 1.15 grms. of crystallised magnesium sulphate were added to some of the zinc solution, made strongly alkaline with ammonia, sodium phosphate added, and after standing about fifteen minutes with frequent stirring, filtered, washed, and the zinc determined in the filtrate.

Zinc taken	0.1490
Zinc found	0.1481

The process gives fairly good results in the presence of iron, calcium, and magnesium, as the following results will show. Where unknown but rather large quantities of solutions of iron (ferri), calcium, and magnesium salts were added to the zinc solution, the whole being strongly alkaline, sodium phosphate was added in large excess, the solution being in a graduated flask which was filled to the mark, mixed, filtered through dry paper, and an aliquot part taken for determining the zinc.

Zinc taken	0.1192 grm.	0.1192 grm.
Zinc found	0.1172 "	0.1172 "

Manganese, however, must be previously separated, best by the nitric acid and potassium chlorate method.—*Journal of the American Chemical Society*, xxiii., No. 7.

PRELIMINARY NOTE ON THE PREPARATION OF BARIUM.*

By EDGAR STANSFIELD, B.Sc.

MANY attempts have been made to prepare metallic barium, but, up to the present, no satisfactory method of obtaining it seems to have been described. There is a general lack of chemical analyses of the products obtained by the various workers, even when they profess to have obtained the metal.

In view of the satisfactory solution by Moissan (*Ann. Chim. Phys.*, 1899, [7], xviii., p. 289), of the difficulties of preparing the allied metal calcium, which can now be obtained in a pure state, I decided to undertake a critical study of the hitherto proposed methods of preparing barium, in the hope of finding some modified or new process which would give good results; care being taken

to check each step by as accurate a chemical analysis as possible.

At present I propose to consider three of these:—

1. *Method of Distillation of Amalgam.*—My results are here in accordance with those of the more modern experimenters (Kern, *Zeits. Anorg. Chem.*, 1898, xvii., p. 284; also 1900, xxv., p. 1; Langbein, "Inaugural Dissertation," Königsberg, 1900). I found that, although it is easy to prepare a crystalline amalgam, containing nearly 5 per cent of barium, by means of the electrolysis of a saturated solution of barium chloride, using a mercury cathode, I was unable to remove all the mercury from this amalgam by distillation *in vacuo*. It is very difficult to completely dry the amalgam without oxidation occurring.

2. *Method of Preparing Zinc Alloys.*—I have tried two methods for this preparation. The first, which consists in electrolysing a fused mixture of barium and sodium chlorides with a molten zinc cathode, was wholly unsuccessful; the second, which is the method used by Caron (*Comptes Rendus*, xlvi., 440), yielded better results. In the best experiments I took 210 grms. zinc, 20 grms. sodium, 120 grms. barium chloride (20 grms. sodium being equivalent to 90 grms. barium chloride); I also added 25 grms. of sodium chloride as a flux. This mixture was heated in a fire-clay crucible until it boiled, and was then allowed to cool. A porous metallic mass was obtained weighing 250 grms., analysis showing that this contained 12 per cent of barium, as well as traces of chlorides and oxides; but that at least some of the barium was present in the metallic state was shown by the freedom with which it decomposed water, especially after it had been powdered.

This product did not seem pure enough to be likely to give good results on distilling off the zinc. The disadvantage of the method of distilling off the mercury or zinc from the amalgam or alloy of barium, seems to be that, at the best, only a product of finely divided material can be obtained; such powdery masses are of very indefinite composition, and, presenting, as they do, so much surface to the action of the surrounding medium, offer considerable difficulty to the working up of a satisfactory product from them.

3. "*The Goldschmidt Process.*"—It appeared therefore advisable to find some method which would give a fused product, such product being likely to have a more homogeneous composition. Since barium evidently has a rather high melting-point, such a process must be one carried out at a high temperature. The Goldschmidt process, whereby oxides are reduced by means of finely divided aluminium mixed with them in an intimate manner, and in which the heat of the reaction, being very large, is generally sufficient to fuse even the alumina formed, was considered likely to give interesting results.

The experiments had to be carried out under reduced pressure, both in order that the charge should not be scattered about by the sudden expansion of the air, due to the rise of temperature, and to prevent loss owing to the formation of barium oxide and nitride, the ease with which these compounds are formed being a great hindrance to all attempts to prepare the metal in the atmosphere.

Description of Apparatus.—Crucibles of Veitsch magnesite of about 200 c.c. capacity were employed; these do not seem to be acted on during the experiment. One crucible generally lasted for two or three experiments before it broke up owing to the sudden changes of heat. Lids were made out of powdered Veitsch magnesite with magnesium chloride solution. The crucible was strengthened by being surrounded by a sheet-iron jacket, and the lid was held down on to the crucible by two brass plates, one below the crucible and the other on the top of the lid, these plates being tightly screwed together by means of three bolts. The crucible, thus encased, was placed inside an iron vessel, over which another iron vessel, inverted, was placed, this being a precaution for the safety of the bell-jar desiccator, inside which the whole apparatus was finally put. Undue heating of the

* Read before the Manchester Literary and Philosophical Society, October 29, 1901. From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, xli., Part 1.

iron vessels by conduction was guarded against by means of asbestos millboard.

The charge is fired by the following contrivance:—Through the sides of the crucible, and near the bottom, were drilled two holes opposite to each other; two aluminium wires were passed through these and joined inside by a bridge of fine platinum wire, which passed through the centre of the starting charge. The aluminium wires were connected by binding screws to two lengths of insulated copper wire, which passed air-tight through the stopper of the desiccator. To fire the charge, an electric current of 2 to 3 ampères was passed through the wires, the platinum wire becoming hot enough to start the reaction.

In the earlier experiments the charge consisted of barium oxide and aluminium, together with a starting charge of barium peroxide and aluminium. It was afterwards found to be more satisfactory to use nothing but the peroxide and aluminium; for not only can the peroxide be obtained in a purer condition, but, the heat of the reaction being greater, a better-fused mass is obtained. The aluminium used was in fine granules, except round the platinum wire, where the flake aluminium was used; it is necessary to strongly heat both sorts before use in order to drive off the fatty matter with which they are always contaminated.

In an actual experiment, all the chemicals to be used and the crucible are strongly heated, and allowed to cool in a desiccator, the charge is then weighed out, and the apparatus fitted up as rapidly as possible to prevent absorption of moisture. The bell-jar desiccator containing the apparatus is then exhausted by means of a water pump, and the charge fired.

After the apparatus has cooled, there remains a grey mass at the bottom of the crucible, which usually contains crystalline flakes of a silver-white metal.

Both the grey mass and the metallic particles decompose water very rapidly. In dry air they do not change, but in moist air they rapidly crumble up, forming a white powder, while if heated in a blowpipe flame they first scintillate slightly, but then becoming coated with oxide they suffer no further action, nor are there any signs of fusion.

In the best experiment, the charge consisted of 100 grms. of barium peroxide, 21 grms. of aluminium (these being in the proportion required by the equation $3\text{BaO}_2 + 4\text{Al} = 3\text{Ba} + 2\text{Al}_2\text{O}_3$), together with 25 grms. of the product of a previous experiment. The product in this experiment was a very hard, almost black mass, which, however, was in parts very rich in crystalline flakes of metal, and also contained some small nodules of metal.

The metallic part contained 63.3 per cent barium, but only 19.3 per cent aluminium, the total being 82.6 per cent. An analysis in another experiment showed 66.6 per cent barium, 29.3 per cent aluminium; total 95.9 per cent.

The analysis of the nodules mentioned above, whilst it gave but 58 per cent barium, was the only case in which the full 100 per cent of barium + aluminium was reached; usually it was impossible to completely separate the flakes of metal from the associated oxide for the purpose of analysis, as the metal was so very brittle.

These experiments seem to indicate that the reaction is reversible, and that it cannot be used to obtain pure barium, but only an alloy of barium with aluminium containing up to about 60 per cent barium.

An endeavour was made to prepare a calcium alloy by this method, but the reaction would not proceed at all. It was also attempted to replace the aluminium by magnesium; in this experiment, the charge taken was only 14 grms. magnesium and 48 grms. barium peroxide, but the reaction was violent and shattered the bell-jar.

I hope to study other methods of preparation, more particularly the electrolysis of barium compounds.

The above work was carried out in the Electro-Chemical Laboratory of the Owens College.

ON TRIVALENT CARBON.

(THIRD PAPER).*

By M. GOMBERG.

It has been shown in the papers published by me on this subject that by the action of metals upon triphenylchloromethane the halogen can be removed quantitatively, and that there results an extremely unsaturated hydrocarbon. From the behaviour of this substance towards halogens and towards oxygen, the conclusion was drawn that it is an unsaturated radicle, triphenylmethyl. It was shown that the same body results whether carbon disulphide, benzene, ether, or acetic ether is employed as a solvent. It was stated that in the case of the first two mentioned solvents the unsaturated hydrocarbon remains in solution, while with ether or acetic ester as a solvent the hydrocarbon separates in the form of large transparent crystals. This crystalline body possessed all the properties of the unsaturated hydrocarbon, and was also identical with the substance which was obtained when triphenylchloromethane in benzene was acted upon by zinc and the resulting hydrocarbon was precipitated from its concentrated solution by means of ether or acetic ester. Facts have since been discovered which necessitate a modification of this view, and I desire to publish the results even in their present incomplete state.

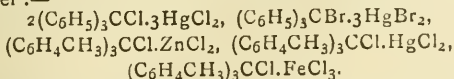
The Action of Zinc in Ether as a Solvent.

When triphenylchloromethane is dissolved in absolute ether and a strip of zinc is introduced, the solution at once turns yellow and a dark viscous mass begins to separate. After a while crystals begin to form which adhere to the zinc and to the sides of the vessel. If the reaction be carried on in a sealed tube it will be noticed that in a few days the black mass begins to diminish in quantity, and in about three weeks it will disappear completely. The solution still remains yellow, but the crystals are colourless. It is impossible to get the ether and the reagents so absolutely free from moisture but that at least a few bubbles of hydrogen will be formed during the reaction (*Am. Chem. Journ.*, xxv., 320). The viscous mass which is formed at the beginning of the reaction is not zinc chloride, but a double salt of it with triphenylchloromethane (*Journ. Am. Chem. Soc.*, xxii., 761). Zinc chloride, I find, is soluble in ether, while the double salt is not. The thick yellow mass which was described under the experiments with benzene is also a double salt of a similar or of identical composition, and not a compound of zinc chloride with benzene, as has been previously supposed. Such a double salt when treated with water would give up all its chlorine to the latter, and this accounts for the somewhat misleading results which were obtained in the estimation of chlorine in the insoluble residue from benzene (*Journ. Am. Chem. Soc.*, xxii., 761). On allowing the ethereal solution to stand for some weeks the double salt is completely broken up by the metallic zinc, but in benzene this does not occur. There is no separation of the double salt when acetic ether is employed as a solvent, for the simple reason that the salt is very soluble in this solvent.

The same double salt is formed with the greatest readiness when a solution of zinc chloride in ether or in acetic ether is added to a solution of triphenylchloromethane in benzene or in absolute ether. All attempts to bring it to crystallisation have failed, but a number of other double salts of triphenylhalogenmethanes, and especially of tritolylchloromethane, were obtained in sufficient purity to establish the remarkable tendency of these halogen bodies towards the formation of double compounds with metallic salts. Substances of the following composition

* From the *Journ. Am. Chem. Soc.*, xxiii., No. 7. The first paper appeared in the *Journ. Am. Chem. Soc.*, xxii., 757; the second in *Am. Chem. Journ.*, xxv., 320.

were obtained, and they will be fully described in a later paper:—



All these compounds are beautifully crystalline, and are characterised by intense colouration, from yellow to red. There is no doubt that the yellow colour which is imparted to the solution when zinc or any metal acts upon triphenylchloromethane is due in a large measure, but not entirely, to the formation of these double salts. The transparent yellow crystals which are formed when a solution of triphenylchloromethane in ether or in acetic ether is treated with zinc are not triphenylmethyl itself, but a compound of that with each of the two solvents respectively.

Compound of the Unsaturated Hydrocarbon with Ether.

Samples of the above-mentioned yellow crystalline compound were analysed from time to time, but the results usually fell from 2 to 3 per cent short of 100 for the sum of carbon and hydrogen. This was at first ascribed to the absorption of oxygen by the unsaturated hydrocarbon during the washing and transference of the material. I then came back to the use of benzene as a solvent. An apparatus was constructed by means of which the benzene solution of the hydrocarbon could be concentrated in a vacuum at 30° C.; ether could then be added, and the crystals that were so formed could be filtered, washed, and thoroughly dried in an atmosphere of carbon dioxide—all these operations being conducted in the same single piece of apparatus, without any rubber connections whatever. The crystalline product obtained in this way is almost insoluble in ether. It was washed with ether from 15 to 20 times to insure the complete removal of the accompanying products, such as triphenylmethane, triphenylcarbinol, &c. The crystals are at first perfectly colourless, but soon turn pale yellow, the colour increasing with standing. Twenty grms. of triphenylchloromethane give about 7 grms. of the insoluble crystalline compound. Molecular weight determinations of this substance were first made and the results were fairly satisfactory as calculated for triphenylmethyl.* An elementary analysis, however, gave the following results:—

0.2884 gm. substance gave 0.9488 gm. carbon dioxide and 0.1900 gm. water.

	Calculated for (C_6H_5) ₃ C.	Found.
Carbon	93.76	89.72
Hydrogen	6.24	7.37

A fresh sample was then prepared in a similar way and was dried over sulphuric acid in a vacuum desiccator (previously filled with carbon dioxide) over night. It gave the following results:—

0.2375 gm. substance gave 0.7832 gm. carbon dioxide and 0.1560 gm. water.

	Per cent.
Carbon	89.94
Hydrogen	7.35

A new sample was then prepared, dried, and analysed in the same day, but the results were almost the same.

0.2447 gm. substance gave 0.8060 gm. carbon dioxide and 0.1585 gm. water.

	Per cent.
Carbon	89.83
Hydrogen	7.25

The next sample was prepared by the addition of a mixture of acetic ether and acetic acid instead of absolute ether, in order to hold better in solution any zinc salts which might possibly have accompanied the previously

mentioned samples. This sample was washed first with acetic ether and then with absolute ether. It looked whiter and more distinctly crystalline than any before obtained, but the analysis gave figures for carbon and hydrogen the sum of which was only 95.67 per cent. The close concordance of the first three samples, and the fact that when acetic ether, which carries almost twice as much oxygen as ethyl ether, is used for precipitating the hydrocarbon, a product proportionately richer in oxygen is obtained, suggested the idea that the substances analysed must be compounds of the hydrocarbon with the solvents.

	Calculated for $2(\text{C}_6\text{H}_5)_3\text{C} + (\text{C}_2\text{H}_5)_2\text{O}$	Found.		
		I.	II.	III.
Carbon	89.93	89.72	89.94	89.83
Hydrogen	7.21	7.37	7.35	7.25

That we have here such a compound is proved by the following experiment:—0.9430 gm. of the ether compound was placed in a platinum boat, and gently heated at 70° C. in a tube, in a stream of carbon dioxide. The loss in weight was 0.1090 gm.

	Calculated for $2(\text{C}_6\text{H}_5)_3\text{C} + (\text{C}_2\text{H}_5)_2\text{O}$	Found.
Loss	13.22	11.56

The escaping ether was easily identified by its odour, and a few droplets were also condensed in a small U-tube which was sealed on to the further end of the tube. The amorphous yellow residue shows all the properties of the unsaturated hydrocarbon. It absorbs iodine with great eagerness; a solution of it, when exposed to air, gives the triphenylmethyl peroxide. An analysis of the residue gave the following results:—

0.1620 gm. substance gave 0.5520 gm. carbon dioxide and 0.1020 gm. water.

	Calculated for (C_6H_5) ₃ C.	Found.
Carbon	93.76	92.93
Hydrogen	6.24	7.05

It remains yet to be settled whether this residue represents pure triphenylmethyl or a mixture of it with some of its decomposition products.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1901.

Prof. J. EMERSON REYNOLDS, F.R.S., President, in the Chair.

(Concluded from p. 10).

178. "The Influence of Salts and other Substances on the Vapour Pressure of Aqueous Ammonia Solution." By E. P. PERMAN.

The author has investigated the effect produced by urea, mannite, potassium sulphate, ammonium chloride, and copper sulphate respectively on the vapour pressure of aqueous ammonia solution by a method similar to that described for sodium sulphate (*Trans.*, 1901, lxxix., 725). The objects of the research were to find (1) the effect upon the pressure of substances which have no direct chemical action on the ammonia, (2) the effect of rise of temperature on copper sulphate ammonia solution, (3) evidence for or against the existence of hydrates in solution.

The conclusions arrived at by the author are:—(1) That salts of the alkalis have a great effect in raising the pressure, but that the effect of other substances which might be expected to have no direct chemical action on the ammonia is either small or nothing.

(2). That copper sulphate forms complexes with

* The determinations were made by the method of the lowering of the freezing-point, in an atmosphere of nitrogen, as carbon dioxide was found to be soluble in benzene to a sufficient degree to impair the results.

ammonia in solution which tend to decompose on heating, especially when the proportion of copper sulphate is small.

(3). The effect of potassium sulphate is similar to that of sodium sulphate in raising the pressure. There is but little reason to suspect the existence of a hydrate of potassium sulphate, as it crystallises without water; consequently it would appear that neither sulphate exists in solution as a hydrate.

179. "The Action of Sodium Hypochlorite on Benzenesulphonanilide." (Preliminary Notice). By J. B. COHEN and J. T. THOMPSON.

In the preparation of the different isomeric dichlorotoluenes (Cohen and Dakin, *Trans.*, 1901, lxxix., 1111), the authors had frequent recourse to the method of chlorination recently studied by Chattaway and Orton (*Trans.*, 1899, lxxv., 1046; 1900, lxxvii., 134 and 789, and *Ber.*, 1899, xxxii., 3573). The authors have found that a very similar reaction occurs with the aromatic sulphonanilides, of which, with Dr. Chattaway's friendly acquiescence, the authors now give a brief notice. Twenty grms. of benzenesulphonanilide were dissolved in 200 c.c. of a solution of sodium hypochlorite (1 c.c. = 0.03 gm. Cl) in the cold and allowed to stand twelve hours. The brown solution was acidified with acetic acid until the buff precipitate re-dissolved, when it was extracted with chloroform. After rapidly evaporating off the solvent, the residual red liquid was digested for an hour with two volumes of glacial acetic acid containing a few drops of concentrated sulphuric acid, until, on pouring into water, a solid substance separated. The new compound was re-crystallised from acetic acid and then from alcohol, when it melted at 129–130°. The yield amounted to 18 grms. of crude or 11 grms. of purified substance.

The mother-liquor contained a small quantity of a semi-solid substance, which became crystalline on standing and after re-crystallisation from benzene and petroleum melted at 116°. This substance is probably the benzenesulphonyl-*p*-chloranilide (m.p. 121°), but it is difficult to free it from oily impurity. The substance melting at 129–130° was analysed, with the following result:—

0.292 gave 14.15 c.c. moist nitrogen at 15.5° and 758 m.m.
N = 5.66.

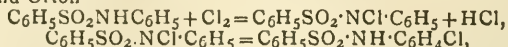
0.3185 „ 0.1764 AgCl. Cl = 13.57.

0.2097 „ 0.1820 BaSO₄. S = 11.93.

C₁₂H₁₀O₂NSCl requires N = 5.23; Cl = 13.27; S = 11.90.

In order to determine the constitution of the substance, it was hydrolysed. Two grms. were heated with about 8 grms. of concentrated hydrochloric acid in a sealed tube to 190° for four to five hours. On opening the tube, there was a strong smell of benzene, the presence of which was confirmed by extracting with light petroleum, nitrating the extract with a mixture of concentrated sulphuric and nitric acids, washing, and evaporating off the light petroleum. On reducing the residue with zinc dust and acetic acid, aniline was formed, and gave an intense violet colouration with sodium hypochlorite solution. The appearance of benzene in the decomposition of the sulphonanilide compound is readily accounted for, seeing that Armstrong and Field (*Ber.*, 1874, vii., 406) and Jacobsen (*Ber.*, 1876, ix., 258) have shown that sulphonic acids are converted into the hydrocarbons by strong hydrochloric acid under pressure. The acid solution, after extracting with light petroleum, was made alkaline with sodium carbonate, and distilled in steam. The distillate was extracted with ether, the ether removed, and the residue dehydrated in vacuo. A yellow oil weighing 0.8 gm. remained. The substance did not solidify on introducing a crystal of *p*-chloraniline, even when cooled in ice; it yielded an acetyl derivative melting at 85–86°, and a benzoyl derivative melting at 102°. This corresponds to *o*-chloraniline, which was prepared from *o*-nitraniline, and then converted into the acetyl and benzoyl derivatives having the above melting-points. In further confirmation, the *o*-chloraniline was heated with benzenesulphonic chloride, and converted into

the sulphonanilide melting at 129–130°, which agrees with the melting-point of the product obtained by the action of sodium hypochlorite on benzenesulphonanilide. The reaction, therefore, probably occurs in two steps, as in the chlorination of the acetyl derivatives studied by Chattaway and Orton—



with the formation mainly of benzenesulphonyl-*o*-chloranilide and a small quantity of the *p*-chloranilide.

Wallach (*Ber.*, 1877, ix., 424) found that benzenesulphonanilide, when heated to 100° with phosphorus pentachloride, yields benzenesulphonyl-*p*-chloranilide, m. p. 121°; but no reference is made to an *o*-compound. The authors have repeated Wallach's work, which they can confirm. The product is difficult to purify, and only a small yield of pure substance could be obtained. From *p*-chloraniline and benzene sulphonic chloride the authors have also synthesised this substance, which melts at 121° as stated by Wallach.

To complete the series, the authors have synthesised the benzene sulphonyl *m*-chloranilide from *m*-chloraniline, which has not been previously described; like the *p*-compound, it melts at 121°. It gave the following result on analysis:—

0.2576 gave 12.85 c.c. moist nitrogen at 13° and 741 m.m.
N = 5.76. C₁₂H₁₀O₂NSCl requires N = 5.23 per cent.

The authors intend to continue the investigation.

180. "The Relationship between the Substitution and the Constitution of Benzeneazo-*o*-naphthol." By J. T. HEWITT and S. J. M. AULD.

Möhlau and Kegel (*Ber.*, 1900, xxxiii., 2858) have shown that benzeneazo-*o*-naphthol reacts with Michler's hydrol (tetramethyldiaminobenzhydrol) to form a condensation product in the same manner as paraquinones and their derivatives. Moreover, the substance obtained acetylates in such a manner that the entering acetyl group attaches itself to a nitrogen atom. The authors mentioned draw the conclusion that benzeneazo *o*-naphthol and its derivatives are of quinone-hydrazone type.

The results obtained by the authors of the present communication are in favour of an oxyazo-formula. Benzeneazo *o*-naphthyl acetate yields aniline on complete fission and no acetanilide. By partial reduction, a hydrazo-compound is obtained melting about 160–165°; the formula C₆H₅·NH·NH·C₁₀H₆·O·COCH₃ is confirmed by the insolubility of the substance in dilute alkalis.

Nitric acid is not a satisfactory substituting agent to use with benzeneazo-*o*-naphthol, but bromine reacts with the azonaphthol in presence of acetic acid and sodium acetate, forming a *monobromo* derivative of m. p. 196°. This substance yields aniline on fission; the bromine therefore enters the naphthol nucleus. From this benzeneazobromonaphthol the *ethyl ether*, m. p. 220° (uncorr.), and *acetyl* derivative, m. p. 146°, have been prepared.

The following substances containing bromine in the benzene nucleus have been prepared for purposes of comparison.

o-Bromobenzeneazo-*o*-naphthol, m. p. 183°. *o*-Bromobenzeneazo-*o*-naphthyl acetate, m. p. 123°. *m*-Bromobenzeneazo-*o*-naphthol, m. p. 211° (uncorr.). *m*-Bromobenzeneazo-*o*-naphthyl acetate, m. p. 112°. *p*-Bromobenzeneazo-*o*-naphthol, m. p. 237–238° (Bamberger, *Ber.*, 1895, xxviii., 1896). *p*-Bromobenzeneazo-*o*-naphthyl acetate, m. p. 141°.

The bromination of benzeneazo-*β*-naphthol is now being studied.

ADDENDUM TO DISCUSSION.

On Messrs. Hall and Plyman's paper, No. 162, on "The Determination of Available Plant Food in Soils by the use of Dilute Solvents."

Dr. DYER pointed out that any process must necessarily be empirical. The actions of the root sap of plants could not be exactly imitated, and much must always depend, not only upon the composition of the solution used, but also upon its volume and the duration of contact. He was

very glad that the 1 per cent citric acid solution had on the whole given more reliable indications of the degree of comparative fertility as regarded both phosphoric acid and potash than did the other acid solutions tried. When he was in America a year ago, he found in use for the determination of "available" phosphoric acid a one-fifth normal solution of hydrochloric acid, but this did not give satisfactory results for potash, and he understood that at that time they had not decided in America what was the best solution to use for potash. As to the limits which he had laid down as indicating need of manurial phosphoric acid or potash, both in his original paper on the Hoos Field soils, and in a paper on the Broadbalk soils (*Phil. Trans.*, 1901, clxiv. B, 235), he had pointed out that the limits which he gave related to cereal crops, and might probably have to be modified with reference to root and other crops. In this direction, much more work was required. Dr. Dyer called attention to some experiments recently carried out by Mr. Ingle, of the Yorkshire College, Leeds, in which he had extracted a large quantity of soil with 1 per cent citric acid solution, and after washing out had grown various crops in it in pot-culture, with and without total or partial replacement of the constituents removed. Some of Mr. Ingle's photographs were exhibited, which showed that the soil when exhausted of its "available" constituents by 1 per cent citric acid solution, was hardly able to support the life of bean plants, but that when the constituents thus dissolved out were replaced the plants flourished abundantly. Mr. Ingle's experiments were not yet completed, but so far they appeared to confirm the practical value of 1 per cent citric acid solution as a reagent in soil analysis.

Dr. J. A. VOELCKER remarked that the experiments of the authors had shown very clearly the influence of one constituent of the soil upon another. Mr. Hall had himself pointed out the variations caused by the presence or absence of lime, and Dr. Dyer had shown how the action of citric acid was influenced by the presence of sodium and magnesium salts, and how irregular were the results when farm-yard manure had been applied to the land. He did not think it was right to take one particular solvent and of one particular strength, and to apply it indiscriminately to all classes of soils alike, nor did he think that the use of hydrochloric acid should be abandoned on the grounds given. That a 1 per cent solution showed, with certain soils, results not consistent with those of certain other solvents or with those of a strong solution of the acid afforded no proof that the acid was an unsuitable solvent. In work on which he had lately been engaged, he had found a 1 per cent citric acid solution useful in many cases, and it was certainly an advance on the older methods, but he was not altogether satisfied with it as yet, and had not found the results to be in all cases consistent with the conclusions arrived at from practical experience of the land. It was not improbable that a distinction would have to be drawn between the two different classes of phosphoric acid present in the soil, the one the phosphoric acid naturally belonging to the soil, the other the phosphoric acid accumulated by repeated manurial applications.

Royal Institution.—On Tuesday next, January 14, Dr. A. Macfadyen, Fullerian Professor of Physiology, R.I., will deliver the first of a course of six lectures on "The Cell, its means of Offence and Defence, Immunity"; on Thursday, January 16, Dr. A. S. Murray will begin a course of three lectures on "Recent Excavations at Delphi and in the Greek Islands"; and on Saturday, January 18, Mr. W. H. Hadow will deliver the first of four lectures (with Musical Illustrations) on "Landmarks in the History of Opera." The Friday evening discourse on January 17, will be delivered by Lord Rayleigh, his subject being "Interference of Sound"; on January 24, Mr. H. G. Wells will give a discourse on "The Discovery of the Future"; and on January 31 Prof. A. Crum Brown one on the "Ions of Electrolysis."

NOTICES OF BOOKS.

The Chemical Analysis of Iron. A Complete Account of all the best known Methods for the Analysis of Iron, Steel, Pig-iron, Iron Ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Producer Gases. By ANDREW ALEXANDER BLAIR. Fourth Edition. London and Philadelphia: J. B. Lippincott Company, 1901. Pp. 319.

OWING to the number of improved methods available, the use of new materials in technical work, and the general advance in chemical knowledge, the author found so many changes necessary to prepare the fourth edition of this work, that he decided to re-write it entirely. In doing this he has substituted chemical terms for formulæ in the text, omitted the marginal notes, and changed the nomenclature to coincide with that in general use. These changes will doubtless recommend themselves to the reader as they all tend towards improvement, an aim to be kept in view in new editions of every work.

After describing the necessary apparatus, reagents, &c., the author goes fully into the methods of analysis of pig-iron, bar-iron, and steel, taking seriatim the estimation of the sulphur, silicon, slag and oxides, phosphorus, carbon, titanium, copper, nickel and cobalt, tungsten, and in fact all the metals, both rare and common, which may be met with in iron. A good deal of attention is paid to the estimation of the carbon in its different forms, both graphitic and combined.

Then follow methods for the analysis of ferrochrome, ferrosilicon, and ferrotitanium; iron ores and their analysis come next in order, then the analysis of limestone, clay, slags, coal and coke, &c., and finally the analysis of gases.

The book is very well printed and bound, and besides its high technical value it forms a handsome volume for the laboratory book-shelf. The table of contents and the index are all that can be desired.

Subject List of Works on Chemistry and Chemical Technology in the Library of the Patent Office. London: Darling and Son, Ltd., and The Patent Office. 1901. Pp. 105.

THE book now before us is one of a series being issued by the Patent Office. Each volume of the series will consist of two parts: (a) a general alphabet of subject headings, with descriptive entries, in chronological order, of the works arranged under these headings; (b) a Key or summary of these headings shown in class order. Under each of these headings the searcher will find entries of all works in the Library which are exclusively devoted to the subject of that heading. Works, however, which deal with the subject of a heading in conjunction with other subjects may have to be looked for under a heading of wider scope.

The present list comprises 885 works (79 serials and 806 text-books, &c.), representing some 3300 volumes, and will, without doubt, be found of great service to searchers and other users of the Library.

Introduction to Physical Chemistry. By JAMES WALKER, D.Sc., Ph.D., F.R.S. Second Edition. London: Macmillan and Co., Ltd. New York: The Macmillan Co. 1901. Pp. 343.

THE short time which has elapsed since the first edition of this book was published in 1891, is good evidence of the favour with which it was received.

Naturally the general aspect of Physical Chemistry has undergone but little, if any, change. The book, however, was never intended as a complete, or even systematic survey of physical chemistry, but more as an explanatory medium. There has always been too great a tendency to keep ordinary chemistry and physical chemistry apart, with the result that the two branches of what may be almost considered the same science have, to a certain extent, interfered with each other in the students' mind,

instead of being mutually helpful. The author's endeavour was to remedy this state of affairs, and, that he has been successful is shown by the increasing demand for his work.

This edition differs from the first one principally in matters of detail, which have been suggested by its use as a text-book.

Among the new matter incorporated in this edition, may be mentioned Daniel Berthelot's method for determining exact molecular weights from the limiting densities of gases, Traube's volume researches, and the position of the recently-discovered atmospheric gases in the periodic system.

The book contains a table of contents and index, and its price is 10s.

Lehrbuch der Chemie und Mineralogie. By Professor G. SIEBERT. Braunschweig: Friedrich Vieweg und Sohn. 1901.

IN this book, which is intended for beginners, the whole ground of inorganic and elementary organic chemistry is covered. The first part contains one hundred experiments introductory to the detailed study of inorganic substances, and renders most simple chemical processes familiar to the student, but the arrangement is not altogether good; many of the experiments would have been better deferred to the second part, which gives a systematic account of the inorganic elements and compounds. In most cases the details of the experiments are clearly and fully described, although the accuracy is not always unimpeachable; we notice, for instance, a method given for preparing copper carbonate CuCO_3 by precipitation of a copper sulphate solution with sodium carbonate, though this error is corrected in the second volume. The third volume deals with organic chemistry and exhibits no particular features to mark it out from many other books of similar scope; it is doubtful, however, whether the order in which the substances are treated might not be improved upon somewhat; and a more systematic arrangement and a fuller explanation of the relationships of the groups of substances to one another would probably tend to give the student a simpler, and at the same time a wider grasp of the subject.

CORRESPONDENCE.

THE VOLUMETRIC ESTIMATION OF MANGANESE.

To the Editor of the Chemical News.

SIR,—Messrs. Ibbotson and Brearley, in their letter to the *CHEMICAL NEWS*, vol. lxxxiv., p. 302, have overlooked the fact that results are given in the original paper on the above subject (*Trans. Chem. Soc.*, 1895, p. 268,) which establish the accuracy of our methods under the given conditions. The point they have now brought forward relating to ferromanganese is therefore already answered.

To sum up the main issues, Messrs. Ibbotson and Brearley have instanced no error in our methods when worked according to the simple instructions contained in the papers. The rare metals occasionally present in small quantities in iron ores, and which pass into the crude iron, cause no appreciable error in the estimation of the manganese. Whilst failing to show that their objection to hydrogen peroxide has any practical bearing except in special steels, they have not met the objection I raised to the employment of ferrous sulphate. The results they quote for their modification are not of the high degree of accuracy established for our method (*CHEMICAL NEWS*, vol. lxxxiv., p. 210), and until they produce evidence that their modification is at least as accurate as ours, and that it is accurate in the analysis of the special steel, they can hardly expect it to meet with the general acceptance of chemists. They have overlooked the fact that one of our methods, although very simple, clean, and rapid,

provides for the analysis of wrought-iron, steel, and pig-iron; they have dealt chiefly with the analysis of special steels. Hydrogen peroxide indicates the presence of the important rare metals in the special steels and no error is likely to occur in the estimation of manganese in these, for special methods of analysis may be applied to them.—I am, &c.

HUGH RAMAGE.

St. John's College, Cambridge,
January 6, 1902.

ON THE MUTUAL ACTION OF ALUMINA AND FERRIC OXIDE AT INCIPIENT WHITE HEAT.

To the Editor of the Chemical News.

SIR,—In connection with Dr. Warth's article on this subject (*CHEMICAL NEWS*, vol. lxxxiv., p. 305), I should like to draw attention to the effect of ferric oxide upon zinc oxide at a red heat. If the two oxides be ground together in a mortar and heated in a porcelain crucible over a Bunsen burner, the colour of the mixture becomes paler, and a portion of the zinc oxide is rendered insoluble in carbonate of ammonia, a fact which proves, I think, that combination of some sort has taken place between the oxides. There is not the slightest evidence of anything approaching fusion.

The amount of zinc oxide rendered insoluble varies with the temperature employed. A mixture of equal quantities of the two oxides heated for half-an-hour over a Bunsen flame and then extracted with ammonium carbonate, retained 27.5 per cent of the zinc oxide in insoluble form. After further heating for one hour over the blowpipe 42.5 per cent became insoluble. In the case of a mixture of 1 part ferric oxide and 4 parts zinc oxide, the strong red colour of the mixture changed after half-an-hour over the Bunsen flame to a golden-brown.

To a less extent this compound resists the action of sulphuric acid. Where highly pyritic or ferruginous zinc biendes have been roasted "dead," a considerable percentage of the zinc will be found to be insoluble in 10 per cent sulphuric acid, and this percentage will vary with the temperature employed. Unless combination has occurred between the two oxides this insolubility of the zinc oxide is difficult to explain.—I am, &c.,

GILBERT RIGG.

76, Bryn Road, Swansea,
December 31, 1901.

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Society of Arts, 8. (Cantor Lectures). "The Purification and Sterilisation of Water," by Samuel Rideal, D.Sc., F.I.C.
- TUESDAY, 14th.—Royal Institution, 3. "The Cell—its means of Offence and Defence—Immunity," by Allen Macfadyen, M.D., B.Sc.
- WEDNESDAY, 15th.—Society of Arts, 8. "Elliptographs," by Frank J. Gray, Assoc. M. Inst. C.E., F.R. Met. S.
- THURSDAY, 16th.—Chemical, 8. "Myricetin" (Part II.), by A. G. Perkin. "The Colouring-matters of Green Ebony," by A. G. Perkin and S. H. C. Briggs. "An Investigation of the Radio-active Emanation produced by Thorium Compounds" (I.), by E. Rutherford and F. Soddy.
- Royal Institution, 3. "Recent Excavations at Delphi and in the Greek Islands," by A. S. Murray, LL.D., F.S.A.
- FRIDAY, 17th.—Royal Institution, 9. "Interference of Sound," by The Rt. Hon. Lord Rayleigh, M.A., F.R.S., &c.
- SATURDAY, 18th.—Royal Institution, 3. "Landmarks in the History of Opera" (with Musical Illustrations), by W. H. Hadow, M.A., Mus. Bac.

AMYLIC ALCOHOL, ETHERS. AMYLACETATE.

FABRIEK VAN CHEMISCHE PRODUKTEN,
SCHIEDAM (HOLLAND).

THE CHEMICAL NEWS.

VOL. LXXXV., No. 2199.

NOTES ON QUANTITATIVE SPECTRA OF BERYLLIUM.*

By W. N. HARTLEY, D Sc., F.R.S.,
Royal College of Science, Dublin.

IN a quantitative examination made in 1885 of all the known methods of separating beryllium from aluminium and from iron, the various precipitates obtained were dissolved and diluted to a known volume corresponding with the amount of bases in solution.

The solutions were spectrographically examined, and the photographs compared with others taken from solutions containing accurately weighed quantities of pure beryllia. The coil used was capable of giving a 5-inch spark in air. In place of a Leyden jar a pane of glass coated on each side with a square foot of tin-foil was used. The electrodes (*Phil. Trans.*, 1884, Part I., p. 49) were Ceylon graphite as in other experiments, the sole impurity in which was a trace of magnesium.

The accompanying tabulated statement gives the wave-lengths of the lines, together with a description of the spectra photographed from solutions of different strengths.

The actual length of the line 2478·1, as rendered by solutions of 0·00001 per cent and 0·000001 per cent strength, is, in the former, 0·07, and, in the latter, 0·05 of an inch. The normal length of the line at this part of the spectrum is 0·22 of an inch. The quantity of substance yielding this spectrum is equivalent to one-millionth of a milligramme of beryllium. As I have pointed out in the case of magnesium (*Phil. Trans.*, 1884, Part II., p. 325), so also is it with beryllium, that the sensitiveness of the spectrum reaction may be increased ten thousand-fold by using a larger coil and more powerful condenser, but leaving the striking distance between the electrodes unaltered. The coefficient of complete extinction was, therefore, practically not attainable for all the lines, or, in other words, the sensitiveness of the reaction is almost without limit.

It will also be seen from my description of the spectra, which have been quite recently re-examined, that the coefficient of extinction of the two lines λ 3130·3 and 2478·1 had not been reached by the dilution specified.

A number of thin sections of the Dublin granite containing microscopic crystals of hexagonal form were examined some years ago. The crystals were supposed to be apatite, but a very carefully executed analysis disclosed the fact that the proportion of phosphoric acid contained in 20 grms. of the rock was almost infinitesimal, and that on warming thin sections, in which the hexagonal crystals were visible, with nitric acid and ammonium molybdate, no deposit of yellow ammonium phosphomolybdate could be detected by the microscope. A spectrographic analysis showed that these crystals were really beryls, and similar crystals a millimetre in length were picked out of the granite. They were found to contain between 10 and 11 per cent of beryllia. Since then beryllia has been separated from the alumina of feldspar obtained from the granite in Glen Cullen in proximity to a vein of coarse granite in which beryls were found by Dr. John Joly.

From numerous experiments on the analytical processes employed in the separation of beryllia from alumina it was found that it remained combined with the sesquioxide bases in so persistent a manner as to lead to the belief

Beryllium
wave-lengths
(Rowland's scale).

STRENGTH OF SOLUTIONS OR DEGREES OF DILUTION SHOWN BY PER CENT OF BERYLLIUM.

	1 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.	0·0001 per cent.	0·00001 per cent.	0·000001 per cent.
3322·3	A continuous line.	Half of the line is much weakened.	A very short line.	A faint indication.	Extinct.	Extinct.	Extinct.
3130·3	A continuous line.	A continuous line.	One-half of the line weakened.	One-half of the line weakened.	Line shorter by one-half.	One-half the line still strong.	Nearly one-half, still strong.
2649·8	A continuous line.	Half of the line is weakened.	A very short line.	Very short line.	A dot merely.	A dot.	A dot.
2493·6	A continuous line.	Half of the line is weakened.	Very short line.	Very short line.	A very faint dot.	A dot, scarcely visible.	A dot, scarcely visible.
2478·1	A continuous line.	A continuous line.	A short line.	A very fine short line.	Very short line.	A very fine short line.	A very fine short line.

* A Paper read before the Royal Society, December 5, 1901.

that ordinary alumina might be found more often than not to contain traces of beryllia, particularly as there is no easily applied chemical test for detecting its presence in small quantities, nor a simple means of separating it. It has, however, been found that such is not the case, though gallium has been ascertained to be present in almost all minerals which contain aluminium. As they belong to the same group, the two elements aluminium and gallium may be expected to form isomorphous mixtures, which would account for their being so constantly associated in nature; but the position of beryllium in the periodic system of classification shows that a similar behaviour with that element is scarcely probable.

ON AN INTEGRAL METHOD FOR
THE DESTRUCTION OF ORGANIC MATTERS,
APPLICABLE TO THE
SEARCH FOR MINERAL POISONS,
ESPECIALLY ARSENIC AND ANTIMONY.

By G. DENIGÈS.

BESIDES the method of destruction by means of a large proportion (30 per cent) of bisulphate of potassium, that G. Pouchet has applied to the detection of small quantities of lead buried in a large mass of organic matter, attempts have been made of late years to integrally destroy such matters, so as to be able more especially to introduce the whole residue from the operation directly into a Marsh's apparatus for the search for arsenic and antimony.

In this way Nikitin and Igfsky dried the organs at 110–115°, and then heated the material with about ten times its weight of concentrated sulphuric acid in a Kjeldahl flask. It requires at least two or three days, and sometimes even four or five days of continuous boiling with acid to obtain complete decolouration.

It is hardly necessary to point out the extreme impracticability of this method; besides the very considerable time required for its performance, the great and dangerous risk of breakage which is always present, and the enormous quantity of sulphuric acid which has to be used (2 kilograms for only 200 grms. of organic matter), we are working with a reagent which for a long while remains strongly reducing, and thus we run the risk of losing arsenic in the form of As_2O_3 , especially in the presence of chlorides. Finally, besides these objections, if the process could even be properly used for an isolated case, it could not be made applicable to a systematic series of destructions.

We have succeeded, without the risk of any loss, in destroying various anatomical samples in a few hours by making use of the following process which is absolutely general in its application, and can even be used for the destruction of the cacodylic molecule which has such great resisting power to other methods of attack; this method, therefore, appears to us capable of being of great service in toxicology and in the elimination of mineral poisons.

This method utilises in the first place the curious oxidising action of the salts of manganese in a nitric medium, discovered by Villiers and applied by that chemist, but under conditions slightly different to ours, to the partial destruction of organic matters, and terminates by the combined action of sulphuric and nitric acids. The following is a detailed description of the process:—200 grms. of the material, in fairly large pieces, are introduced into a porcelain dish of 2 litres capacity, with 200 c.c. of nitric acid at about 40° B. (density 1.39 to 1.40), and 5 c.c. of permanganate of potassium at 2 per cent; this is heated over a Bunsen burner, the dish resting on a sheet of iron 2 or 3 m.m. thick, 11 to 12 c.m. diameter, and perforated at the centre with a hole 4 c.m. diameter.

After from a quarter to half-an-hour, according to the state of division of the mass and the nature of the organs (it is more rapid with muscle, but less so with the viscera, liver, &c.), the disaggregation is complete, and the froth at first formed gives way to tranquil boiling. If the froth, which is particularly abundant in the case of parenchymatous (liver, kidneys) organs, on account of the urea or ammoniacal products which they may contain, and especially with skins and hair which are rich in carbonate of lime, if this froth is in any danger of running over the sides of the dish, it must be broken up with a stirring-rod, or the flame should be withdrawn for a time; this is often necessary with epithelious organs, more particularly skins and hair. In the latter case, the length of time required for the disaggregation will slightly exceed the limits we have mentioned above.

On reaching this stage the mass is placed in a 1 litre porcelain dish, the large dish is rinsed with 100 c.c. of nitric acid at 40° B., which is heated to about 50–60° in the dish itself, and then poured into the 1 litre dish; the same is repeated with 100 c.c. of warm water for the final rinsing of the large dish.

All the liquid, as well as the supernatant fat, being collected together in the 1 litre dish, this latter is covered with a large glass funnel, the edge of which reaches to the commencement of the lip of the dish, and of which the stem has been cut down to about 1 or 2 c.m., leaving an opening of about 15 to 20 m.m. diameter; the whole is then raised to gentle boiling, when a mixture of nitrous fumes, nitrogen, and carbonic acid is given off.

The heat is continued for at least two hours, as it is necessary to reduce the volume to a little less than 100 c.c.; if there is time it is preferable to lower the flame, and to allow the attack to continue for four or five hours. In any case care must be taken never to evaporate so far that the mixture commences to blacken; by stopping when the volume of the residue is still about 70 or 80 c.c. this can be prevented.

If, however, this should happen during the course of the operation, it would be necessary to stop at the first symptom, of browning, and to add to the mass 10 to 20 c.c. of nitric acid, and then heat again until the liquid is entirely clarified.

When the desired volume is reached (70 to 80 c.c.) the funnel and the flame are both removed, then, without any time for cooling, 100 c.c. of pure sulphuric acid are added rapidly, and stirred with a glass rod;* reddish-brown fumes are rapidly evolved, then, as they cease coming off, the mass becomes brown. We then wait about two minutes from the time when this colouration appears, and add 5 c.c. of nitric acid in a fine stream, which must be run in from a pipette at the centre and close down to the surface; this operation is repeated four times in all, using about 20 to 25 c.c. of nitric acid. After the last addition the whole is heated strongly for four or six minutes, so that the sulphuric acid will thoroughly attack the supernatant fatty matters; the flame is then removed, and then, three times in succession, at two minutes interval, 5 c.c. of nitric acid are added, operating as described above. This done the funnel is replaced, and heat again applied, but always with the sheet-iron disc under the dish so as to ensure the sulphuric acid boiling.

From this moment, every two or three minutes, we pour, a drop at a time, 50 to 60 drops of nitric acid at 40° B., using a capillary funnel passing through the hole in the top of the inverted large funnel, and letting the end reach to about 1 c.m. of the surface of the material operated upon. After each addition the funnel should be raised a little to prevent superheating and cracking from the cold nitric acid when the dropping is no: quite continuous.†

* When the fatty residue is very considerable, we are sometimes, but only in exceptional cases, obliged to exceed this quantity of acid; the important point being to leave the mass fluid, even after attacking with sulphuric acid and after intense blackening.

† Time can be saved and the operation made less tedious by adding the nitric acid in a continuous manner with the aid of a

After about ten to fifteen additions of acid, or even more in the case of very fat viscera, the residual liquor, even when strongly heated after all the nitric acid has been driven off, takes first a reddish-yellow and then a bright yellow colour. The excess of sulphuric acid is then driven off by evaporation, so as to bring the final volume of the residue down to 10 or 15 c.c. During the evaporation 50 or 60 drops of nitric acid must again be added, at least four or five times, through the capillary funnel. After cooling, the residue which ought to be colourless or at most barely yellow, is treated with 100 c.c. of water; nitrous fumes are generally given off owing to the hydrolytic decomposition of a nitro-sulphuric acid formed during the course of the operation, and of which the presence is a certain, if not a necessary indication, of the complete destruction of the organic matter. After boiling to completely drive off these fumes, the whole is again cooled, and enough distilled water added to give a dilution of a tenth, by volume, of the final acid residue, which should have been carefully measured before the addition of water.

In this manner a perfectly colourless liquid is obtained which contains integrally the whole of the arsenic, antimony, and mercury present in the original substance under examination, as we have proved by our experiments, on numerous occasions.

Very frequently (even apart from bone and tissues rich in calcareous material, such as epidermic products) the liquid holds in suspension a small quantity of crystalline mineral residue, generally consisting of sulphate of lime, and sometimes of ferric sulphate with anatomical fragments rich in ferruginous matter (liver, &c.); in the latter case the boiling with sulphuric acid is sometimes attended with bumping, the crystalline grains being much less soluble than the sulphate of lime in concentrated acid.*

These mineral residues, unless they are very abundant, when they can be separated by filtration through a plug of cotton-wool or gun-cotton, in no way interfere with the direct introduction of the liquid containing them into a Marsh's apparatus; neither do the extremely faint traces of nitric products which may be present in the liquid; they can, however, be removed if desirable before the final addition of water by the aid of oxalic acid, urea, or sulphate of ammonium added directly in the form of powder, to the colourless, boiling sulphuric residue.

The above method is absolutely general in its application; we shall now, in addition, proceed to point out the slight variations which can be introduced for the destruction of such bodies as glycerin, cacodylic products, &c., which are reputed difficult to destroy, or in other important instances such as bone, hair, skin, milk, urine, &c.

Destruction of Epidermoid Materials and Bone.

With hair treated by the general method, after a few minutes in the cold, a lively effervescence takes place; the attack goes on by itself without the aid of heat, and the material is practically dissolved after fifteen or twenty minutes. It is then heated; the amount of nitric acid used should be, for the same weight of material, double the ordinary proportion. Liquefaction once obtained the operation is completed as above.

With skins, analogous phenomena are observed, and the manipulation is the same.

With bone, when once the nitric attack is finished and the reduction of the volume to 70 or 80 c.c. effected, the whole is cooled, filtered through cotton-wool or gun-cotton, washed with dilute nitric acid, retaining the fat, which must be washed with great care. The filtrates are

siphon fitted with a glass tap, having the short end plunged into the acid and the long end drawn out fine, passing 1 drop every two seconds through the capillary end; this can easily be adjusted by means of the tap.

* It is obvious that when the substances destroyed contain a sufficient quantity of lead, barium, or strontium, these metals will be found, at least in part, in the residue in the state of insoluble sulphates.

diluted with a large quantity of water, precipitated with a slight excess of sulphuric acid, and filtered through cotton-wool or gun-cotton, or even glass-wool. The precipitate of sulphate of lime is washed until it is perfectly white and the washings colourless; the filtrates are then again concentrated down to 70 or 80 c.c., the filtered fat added, and 100 c.c. of sulphuric acid (for 200 grms. of bone); it is then heated, and the operation completed as in the general case, always taking care not to push the evaporation too far, and to leave, besides the phosphoric acid, 10 to 15 c.c. of sulphuric acid in the residue, which can be diluted proportionally.

Destruction of Milk.

To 400 c.c. of this liquid, placed in a 1 litre porcelain dish, we add 200 c.c. of nitric acid at 40° B., 5 c.c. of 2 per cent permanganate of potash, raise to gentle boiling, and evaporate down to 70 or 80 c.c., after having covered the dish over with the large funnel with a short stem already described; while still warm 100 c.c. of sulphuric acid are added, and the operation completed as in the general case. In this manner we have easily succeeded in detecting 0.5 m.grm. of mercury in 1 litre of milk by using Merget's method, which consisted of immersing for twenty-four hours in the liquid diluted with water, a copper-wire which has been washed in water, alcohol, and ether, and then dried, and then placing it in contact with paper soaked in ammoniacal nitrate of silver for half-an-hour or an hour.

Destruction of Urine.

500 c.c. of urine are boiled in a 1 litre porcelain dish with 100 c.c. of nitric acid at 40° B., and 5 c.c. of 2 per cent permanganate of potash. The whole is covered over with a large funnel as soon as the froth which is first formed disappears.

When the volume is reduced to 100 or 150 c.c. we add a further 100 c.c. of nitric acid and heat again until the volume is reduced to 60 or 80 c.c.; then, while still warm, 25 c.c. of pure sulphuric acid are added (50 c.c. in the case of diabetic urines); this is then heated until strong blackening takes place and white fumes are given off; the destruction and decolouration of the mass are then completed by nitric oxidation as in the general case.

We have observed that the presence of a large proportion of chlorides in urine (up to 12 grms. per litre, that is to say 6 grms. in the ordinary sample of 500 c.c.) does not lead to any loss of arsenic under these conditions. Still, if we wish to do away with the influence of these salts, we must work on a sample never containing more than 5 or 6 grms. of chlorides, and dilute to 500 c.c.; or still better—to 700 c.c. of urine we add 20 c.c. of nitric acid and as many times 1.5 grms. of powdered nitrate of silver as there are grms. of chlorides (expressed as NaCl) per litre of the urine examined. This is well shaken several times, allowed to settle, and 5.15 c.c. of the clear liquid decanted or filtered off, representing 500 c.c. of the urine under examination, which is then treated as above.

Destruction of Wine.

In a two-litre dish, one litre of red or white wine is reduced by boiling to about 300 c.c., then, removing the flame, we add 5 c.c. of 2 per cent permanganate of potash in a very fine stream while continually stirring, and 100 c.c. of nitric acid at 40° B. When the effervescence which is generally produced has abated, the mixture is placed in a one-litre dish and covered with the large funnel with a short stem. It is then boiled continuously and steadily until the volume is reduced to 50 or 60 c.c.; without removing the flame 30 c.c. of pure sulphuric acid are then added. After the blackening of the mass and expulsion of the nitrous fumes, nitric acid is added in several portions and the operation is continued and terminated as in the general case.

When we have to deal with a sweet wine, the proportions of nitric and sulphuric acids is doubled.

Destruction of Glycerin.

One hundred grms. of glycerin are placed in a 1 litre porcelain dish, with 500 c.c. of a mixture of equal volumes of nitric acid at 40° B., and water; then add 5 c.c. of a 2 per cent solution of permanganate of potash. Heat over a Bunsen burner, using the perforated iron plate.

Between 90° and 95° a lively reaction takes place with an abundant disengagement of reddish-brown nitrous fumes. The flame is immediately removed, but in spite of that, the energetic chemical reaction quickly raises the temperature to above 100°. When it has cooled down to about 90°, heat is applied again by means of a very small flame, so as to keep the temperature between 90° and 95°, without, however, surpassing the latter point; it is then covered with the large funnel described above.

The reddish fumes diminish considerably, and at last a moment arrives when the attack goes on regularly with tranquil effervescence and barely noticeable disengagement of nitrous products.

When the volume of the liquid is reduced to 75 or 100 c.c., 500 c.c. of the already mentioned hydronitric mixture are added. Heat is again applied until abundant reddish fumes come off, the funnel is replaced, and the temperature brought to and maintained at about 95° until the volume is again reduced to about 100 c.c.

At this point 25 c.c. of sulphuric acid are added, while still heating, and the funnel put on again. If nitrous fumes come off very freely the flame is removed immediately to allow the action to slacken. If the fumes do not come off very abundantly the heating is continued.

In both cases, however, a moment arrives while still heating, when the evolution of nitrous fumes ceases and the mass becomes decolourised; soon after it becomes yellow, then brown, and gives off an odour of caramel.

When it has turned black the decolouration must be effected by means of nitric acid and the operation completed as in the general case. The destruction is effected in a most perfect manner.

Destruction of Methylene Blue.

Twenty-five grms. of methylene blue are heated in a 1 litre porcelain dish with 75 c.c. of nitric acid at 40° B., 25 c.c. of water, and 5 c.c. of 2 per cent permanganate of potash, the whole being covered with the large funnel.

After boiling for half an hour, 50 c.c. of nitric acid are added, being poured round the sides of the dish.

Heat is applied until the blue colouration gives way to a reddish tint and the volume is reduced to about 50 c.c.

At this moment 25 c.c. of concentrated sulphuric acid are added, and the operation terminated as in the general case.

Destruction of Cacodylic Molecule.

If we suspect the presence of cacodylic products in the organic substances it is sought to destroy, after having operated as described in the general case, or in any one of the particular ones just described, and having arrived at a final volume of about 15 c.c. in the latter part of the operation, we add 5 or 6 grms. of pure nitrate of potash and heat until the excess of free sulphuric acid is driven off, and fused bisulphate of potash formed. After cooling, the saline mass is taken up with 100 c.c. of boiling 10 per cent sulphuric acid in water; this is again allowed to cool after complete solution.

By thus destroying 200 grms. of horseflesh containing 0.08 gm. of pure anhydrous cacodylate of soda the whole of the arsenic was recovered, either by the ring method, or by the nitrate of silver method, without any garlic odour being noticed during the destruction and subsequent hydration. Further, the quantity of bisulphate of potash present in the substance is too small to interfere with the direct introduction of the material into the Marsh's apparatus and form crystals of potassio-zinc sulphate on the zinc.

We may add, in conclusion, that if it is desired to employ the process now described and to be certain of

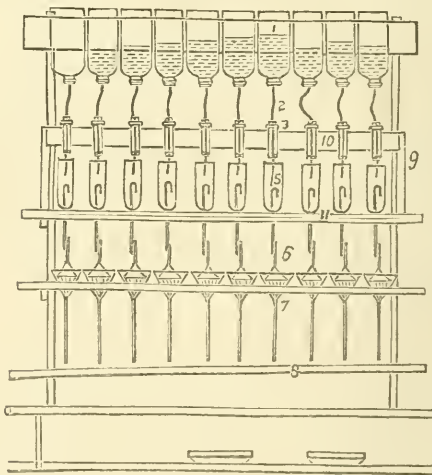
success, it suffices to make one preliminary trial with either beef or horseflesh, and to remember that it is more especially the additions of nitric acid to the sulphuric acid heated sufficiently to emit thick white fumes, which effect the complete destruction of the material. The use of the funnel, as described, is also indispensable; it can easily be handled with a strong pair of spring tongs with which the stem is held, and which for this reason therefore must not be cut too short.

It is well understood that the operations should always be carried out in a glazed fume cupboard with a strong draught, with just a small opening giving access to the apparatus.—*Bull. Soc. Chim.*, Series 3., xxv., No. 22.

AN AUTOMATIC FILTER-WASHER.

By J. M. PICKEL.

THE apparatus shown in the accompanying cut consists of a battery of ten washers. The parts of each washer are:—A reservoir, 1, to contain the liquid with which the washing is done. A rubber tube, 2, provided with two thumb-screw clamps, 3, leading from the reservoir to the delivery vessel. A delivery vessel, 5, provided interiorly with a small syphon, which delivers the washing liquid intermittently in small portions on the substance being washed. A larger funnel, 7, containing the filter. A smaller inverted funnel, 6, covering the substance. The object of this funnel is, while it prevents spattering, to throw the liquid around over the edge of the filter-paper, thus insuring that it be washed from the top downward at each delivery. It should be of such a diameter as almost, but not quite, to cover the filter-paper. A trough, 8, which conveys the washings, in case they are not wanted, into the waste pipe. A supporting frame, 9, 10, 11.



The apparatus is operated thus:—The substance to be washed having been placed on the filters and covered with the inverted funnels, and the lower clamps having been closed, each reservoir is provided with a measured quantity of liquid adequate to the washing. To facilitate the measuring, the reservoirs should be graduated once for all. By means of the lower clamp discharge the liquid rapidly into the delivery vessel until the syphon overflows, then regulate (by the lower clamp) the flow, so that the liquid shall fall, drop by drop, into the delivery vessel at such a rate that the syphon shall not overflow till after all the liquid has passed out of the filter. This regulation insures the intermittent washing of the filter with entirely fresh portions of liquid at each delivery, and, with a little

practice and patience, can be accomplished in about ten to fifteen minutes for all ten of the washers. After the apparatus is once regulated, it requires no further attention—may be left going over night.

The upper clamp is not necessary, but is at times convenient; for example, if for any reason it is desired to stop the flow of liquid before the washing is completed, this is effected preferably by the upper clamp, thus leaving the "set" of the lower clamp undisturbed. The efficiency of the machine depends upon the ease and accuracy with which it may be regulated. The screw of the regulating clamp must, therefore, have a fine thread; the clamp must be firmly fixed in place, otherwise the merest touch will sometimes change the rate of flow. The washer at the extreme left of the cut shows a method of securing this fixedness. The clamps and attachment are there turned through an angle of 90°. A piece of wood about two inches long and of rectangular section passes through the clamp. Transversely across the back of the piece of wood are shallow grooves in which the clamps fit. These pieces are firmly attached by screws to the frame-piece marked 10. Small wire brads, one just above and one just below the clamp, and each slightly pressing against it, are driven a short way into the wood, completing thus the steadiness of the clamps. The arrangement here described is satisfactory; but doubtless a tube and glass cock, capable of delivering small drops (after the manner of a good burette) would be preferable.

The quantity of water delivered at each discharge of the syphon should, of course, be sufficient to cover the substance, but not enough to flood the filter to overflowing. The capacity of the delivery vessel may be varied by adding to or taking from it, small glass beads, coarse sand, or fragments of glass. It is evident that, if the syphon is on the outside of the delivery vessel (after the manner of a Soxhlet extractor), the capacity of the vessel may easily be varied from its greatest volume down to an almost vanishing quantity by shoving down into it a tube closed at its lower end (a test-tube for example); a small plug of rubber wedged in between would hold the tube at any desired level. A Soxhlet can be utilised as a delivery vessel; one in possession of the writer whose normal maximum delivery is 43 c.c. can, in the manner just described, be instantly made to deliver any lesser quantity down to 7 c.c.

As is seen from the cut, the delivery vessels in the apparatus here described are what are known as carbon filters, for Gooch filters. Their dimensions are, for the large end, about 2 to 3 inches in length and 1½-inch internal diameter, small or stem end, about 2 inches in length and ¼-inch internal diameter. The long arm of the syphon passes through the stem, and is made water-tight by a short piece of rubber tubing. They were regulated once for all to deliver about 10 to 15 c.c. The syphons should be well made, particular care being taken that they are not flattened, or contracted, at the bend. A syphon thus contracted requires, especially when it becomes somewhat soiled internally, and does not readily wet, considerable pressure to force the water over; it will therefore vary considerably in the volume of liquid that it delivers at an overflow. For this reason also a narrow tall delivery vessel is to be preferred to one of larger diameter—there is less variation in the quantity of liquid delivered at each overflow of syphon in the former than in the latter. A diameter (internal) of not over an inch—of even three-quarters of an inch or less if practicable—is to be recommended. I especially call attention to this, because I found that some of my delivery vessels, which were set to deliver about 10 c.c., would, owing to the causes here detailed, sometimes cause my filters to overflow (I was using quite small, 9 c.m. filters). The reservoirs in this apparatus were made by cutting off, near the bottom, pint bottles. Small percolators would be neater.

The combination here described as an automatic filter-washer is, so far as the writer knows, new. At any rate, it was new to him, and devised by him for washing water-

soluble nitrogen (more especially nitric and ammoniacal nitrogen) out of mixed commercial fertilisers. It was used the past winter and spring for that purpose in the analysis of several hundred samples, and was found entirely satisfactory and a valuable labour-saver. Two nitrogen determinations were made in each case, one of total nitrogen, the other of residual nitrogen after washing with 300 c.c. of distilled water.

There would seem to be no reason why this washer might not be used, with equal advantage, to take water-soluble phosphoric acid out of commercial fertilisers. A comparison of its work in this matter with the method of washing commonly practised, was made with the following result on ten different fertilisers:—

Per cent.	Water soluble P ₂ O ₅ .		Difference.
1	6.65	6.42	0.23
2	4.55	3.78	0.77
3	9.51	8.92	0.59
4	9.31	8.75	0.56
5	8.04	7.88	0.16
6	9.24	8.65	0.59
7	5.97	6.10	—
8	6.10	5.68	0.42
9	5.06	4.72	0.34
10	6.03	5.42	0.58

The percentages in the first column were obtained in the washings from the automatic washer; those in the second column were obtained in the usual way by directing a jet of water on the substance, and thoroughly stirring up at each washing. Two grms. of fertiliser were taken in each case, and the same quantity (or about the same quantity), a little less than 300 c.c. of water, was used for washing in each case. In all except one case, the automatic washer took out more phosphoric acid than the usual method. This is all the more remarkable inasmuch as the washer does not stir the substance to any appreciable extent. The explanation of the difference is perhaps to be found in this circumstance; the washer delivered the water in small portions of about 10 c.c. at a time, whereas in the other case 30 to 40 c.c. were used, the filter being larger; it thus came about that in the first case the samples got three to four times as many separate washings as in the second. There was this further circumstance:—The machine, once set going, keeps up the work to the end, thus finishing the operation in a shorter time than did the hand washing, where the chemist was diverted by other operations which he was looking after at the same time. Such being the case, the phosphates were in contact with the water a shorter time in the first than the second instance, and the monocalcium phosphate had less opportunity (less time) to "revert."—*Journal of the American Chemical Society*, xxiii., No. 8.

Methods of the Formation of Peroxide of Lead.—G. Kasner.—The author has already shown that metaplumbate of lime gives, through the action of heat, peroxidised compounds of lead, of which the lime salts are veritable perplumbates. The orthoplumbate containing water of crystallisation, Ca₂PbO₄.4H₂O, gives the same result. The formation of these peroxidised compounds should not be attributed to a fixation of free oxygen, but to an internal oxidation; that is to say, to a fixation on the lead of oxygen furnished by the molecule of the heated salt. The peroxide of lead is, in fact, produced in the complete absence of free oxygen; for example, in the presence of inert gases or even in vacuo. In the preparation of this peroxide, it is necessary to prevent a too prolonged action of heat, for fear of destroying the molecule formed, with the liberation of the inactive oxygen.—*Arch. d. Pharm.*, vol. cxxxviii., p. 449.

ON THE RELATION OF THE VISCOSITY OF MIXTURES OF SOLUTIONS OF CERTAIN SALTS TO THEIR STATE OF IONISATION.*

By JAMES BARNES, B.A., Dalhousie College, Halifax, N.S.

(Continued from p. 5).

Determination of the Ionisation Coefficients at 25° C. for Simple Solutions.

THE ionisation coefficient for a simple solution is taken to be the ratio of the specific molecular conductivity to the specific conductivity at infinite dilution. Before this ratio could be found for 25° C. it was necessary to determine the values of the specific conductivity at 25° from Kohlrausch's values at 18° (Kohlrausch und Holborn, "Leitvermögen der Elektrolyte," 1898, p. 159, Table 2) by means of Déguisne's (*loc. cit.*) and Kohlrausch and Grottrian's temperature coefficients (Kohlrausch und Holborn, *loc. cit.*, p. 145, Table 1). The concentrations of solutions of the salts for which Kohlrausch gives conductivity values did not in all cases correspond to the concentrations of solutions for which Reyher and Wagner determined the viscosity. In such cases (concentrations 0.25 and 0.125), the values of the specific conductivities at 25° were obtained by interpolation.

Table III. gives both the values of the specific conductivity at 25° C. determined as above from the values at 18°, and the calculated ionisation coefficients at 25°. Only those coefficients are given which are necessary in the calculation of the viscosities. Under copper sulphate are given a few conductivity values of higher concentration, these being necessary for the determination of the ionisation coefficients in the mixtures by the method used. The concentrations are expressed as in Table I., and conductivities in terms of 10⁻⁴ times Kohlrausch's new unit.

Determination of the Ionisation Constants.

Table IV. gives the values of the ionisation constants (*k* and *l*) determined by the method of least squares from the data given in Tables III. and V., the observed values of the viscosity of the four solutions of each salt being used. The relative magnitude and the sign of the ionisation constants would seem to show that the undissociated molecules exert the greater influence in increasing the viscosity, while the free ions have in some cases a diminishing effect.

Results of Calculations on Simple Solutions.

Table V. gives a comparison of the calculated and observed values of the viscosity of simple solutions, the calculated values being determined by expression (1) with the ionisation coefficients and ionisation constants, as given in the above tables. In this table, all the viscosity results are relative to water at 25° C., and the concentrations are expressed as in Table I.

As both Reyher and Wagner regard their results as affected by a possible error of about ± 3 in the third decimal place, it is seen that the agreement between the calculated and observed values for all the salts except copper sulphate is very satisfactory, the differences being well within the limit of experimental error. In the case of copper sulphate, the agreement is not so satisfactory. But it was noticed on plotting the observed values against the concentration that the points do not lie on a smooth curve, and that the point corresponding to the concentration 0.5 is at quite a distance from this curve, which leads one to think that this observed value cannot be correct. The poor agreement in this case might also be partly due to the doubtful value of the specific molecular conductivity

TABLE III.

Concentration.	Specific conductivity at 18° C.	Specific conductivity at 25° C.	Ionisation coefficients at 25° C.
NaCl.			
1.0	744.0	862	0.672
0.5	404.5	469	0.732
0.3	255.6	296	—
0.25	—	252	0.786
0.2	176.4	205	—
0.125	—	131	0.817
0.1	92.5	107	—
KCl.			
1.0	982.0	1128	0.743
0.5	511.5	588	0.774
0.3	315.9	363	—
0.25	—	308	0.811
0.2	215.4	248	—
0.125	—	159	0.838
0.1	111.9	129	—
$\frac{1}{2}$ BaCl ₂ .			
1.0	703	811	0.566
0.5	388	448	0.624
0.3	249	287	—
0.25	—	245	0.684
0.2	173.4	200	—
0.125	—	130	0.726
0.1	92.2	106	—
$\frac{1}{2}$ K ₂ SO ₄ .			
1.0	718.0	827	0.528
0.5	393.5	453	0.578
0.3	253.2	292	—
0.25	—	251	0.640
0.2	177.8	205	—
0.125	—	135	0.690
0.1	95.9	111	—
$\frac{1}{2}$ Na ₂ SO ₄ .			
1.0	508.0	591	0.443
0.5	298.5	347	0.520
0.3	199.8	230	—
0.25	—	201	0.604
0.2	142.8	166	—
0.125	—	110	0.662
0.1	78.4	91.4	—
$\frac{1}{2}$ CuSO ₄ .			
2.631	458	534	—
2.194	421	489	—
1.0	258	297	0.209
0.5	154	177	0.249
0.3	106.5	122	—
0.25	—	107	0.302
0.2	78.4	89.9	—
0.125	—	61.7	0.347
0.1	45.0	51.6	—

TABLE IV.

Electrolyte.	<i>k</i> .	<i>l</i> .
NaCl	+0.11213	+0.089765
KCl	+0.30645	-0.12289
$\frac{1}{2}$ BaCl ₂	+0.20327	+0.061009
$\frac{1}{2}$ K ₂ SO ₄	+0.21347	+0.0088236
$\frac{1}{2}$ Na ₂ SO ₄	+0.30418	+0.13348
$\frac{1}{2}$ CuSO ₄	+0.46500	-0.058144

at infinite dilution used. Thus it seems that for all the salts examined, copper sulphate perhaps excepted, expression (1) gives the viscosity of a solution within the limit of experimental error throughout a concentration range of 1.0 to 0.125.

* Transactions of the Nova Scotian Institute of Science, x., p. 113.

TABLE V.—Viscosity at 25° C.

Concentration.	Observed value.	Calculated value.	Difference.
NaCl (R-yher).			
1.0	1.0973	1.0971	-0.0002
0.5	1.0471	1.0479	+0.0008
0.25	1.0239	1.0236	-0.0003
0.125	1.0126	1.0117	-0.0009
KCl (Wagner).			
1.0	0.9872	0.9874	+0.0002
0.5	0.9874	0.9871	-0.0003
0.25	0.9903	0.9896	-0.0007
0.125	0.9928	0.9933	+0.0005
$\frac{1}{2}$ BaCl ₂ (Wagner).			
1.0	1.1228	1.1228	±0.0000
0.5	1.0572	1.0572	±0.0000
0.25	1.0263	1.0265	+0.0002
0.125	1.0128	0.0125	-0.0003
$\frac{1}{2}$ K ₂ SO ₄ (Wagner).			
1.0	1.1051	1.1054	+0.0003
0.5	1.0486	1.0476	-0.0010
0.25	1.0206	1.0206	±0.0000
0.125	1.0078	1.0090	+0.0012
$\frac{1}{2}$ Na ₂ SO ₄ (Wagner).			
1.0	1.2291	1.2286	-0.0005
0.5	1.1058	1.1078	+0.0020
0.25	1.0522	1.0502	-0.0020
0.125	1.0235	1.0239	+0.0004
$\frac{1}{2}$ CuSO ₄ (Wagner).			
1.0	1.3580	1.3556	-0.0024
0.5	1.1603	1.1675	+0.0072
0.25	1.0802	1.0767	-0.0035
0.125	1.0384	1.0354	-0.0030

(To be continued).

THE CONSTITUTION OF TOURMALINE.*

By F. W. CLARKE.

(Continued from p. 14).

BETWEEN the magnesium tourmalines and the iron tourmalines the closest analogy exists, and the identity of type is absolute. Taking except when otherwise specified, the analyses by Riggs, all the iron tourmalines reduce to mixtures of the following isomorphous molecules:—

- A. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3(\text{AlOH}).\text{Fe}_4\text{H}_4$,
- B. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Ca}.\text{Fe}_4\text{H}_4$,
- C. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{NaH}.\text{Al}_3\text{NaH}_2$,
- D. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{NaH}.\text{Al}_2\text{Na}_2\text{H}$,
- E. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{NaH}.\text{Al}_3\text{Na}_3$

Molecules C, D, and E are evidently identical, except in the varying replacements of sodium by hydrogen. A and B are similarly alike, so that actually only two fundamental compounds are assumed. From the commoner iron tourmalines lime is practically if not quite absent; and these may be interpreted very nearly as mixtures of A and C, such as As_2C_5 , A_7C_5 , &c. If we take the minute quantities of lime into account, the black tourmalines from Brazil and from Stoney Point, North Carolina, correspond to $\text{A}_{13}\text{B}_2\text{C}_9$; that from Auburn, Maine, to $\text{A}_{35}\text{B}_2\text{C}_{27}$, and that from Paris, Maine, to $\text{A}_{10}\text{B}_1\text{C}_9$. It will be noticed that the molecule A is in excess of the other two—a condition which fits the analyses, but which is incompatible with the formula proposed by Penfield and Foote. To satisfy the latter, the number of A mole-

cules should be exactly equal to B+C, giving the ratio Si_4O_{21} or $\text{Si}_6\text{O}_{31.5}$. The analyses in question are as follows:—

	Brazil.	Stoney Point.	Auburn.	Paris.
SiO_2 ..	34.63	35.56	34.99	35.03
B_2O_3 ..	9.63	10.40	9.63	9.02
TiO_2 }	..	0.55	—	—
Al_2O_3 }	..	32.70	33.38	33.96
Fe_2O_3 }	..	0.31	—	—
FeO }	..	13.69	8.49	14.23
MnO }	..	0.12	0.04	0.06
MgO }	..	2.13	5.44	1.01
CaO ..	..	0.33	0.53	0.15
Li_2O }	..	0.08	trace	—
Na_2O }	..	2.11	2.16	2.01
K_2O }	..	0.24	0.24	0.34
H_2O }	..	3.49	3.63	3.62
F }	..	0.06	—	—
	99.52	100.42	100.00	99.89

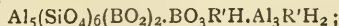
The reduced analyses and their comparison with the calculated composition is as follows:—

Found.	Found.	Calcu-	Found.	Calcu-	Found.	Calcu-
Stoney	Brazil.	lated.	Stoney	lated.	Paris.	lated.
Point.	$\text{A}_{13}\text{B}_2\text{C}_9$.	Auburn.	$\text{A}_{35}\text{B}_2\text{C}_{27}$.	$\text{A}_{10}\text{B}_1\text{C}_9$.		
SiO_2 .	34.10	34.26	34.27	34.75	34.48	34.70
B_2O_3 .	9.98	9.54	9.99	9.56	10.06	8.94
Al_2O_3 .	32.37	32.54	32.36	33.73	33.28	34.82
FeO .	17.33	17.45	17.14	15.99	15.95	15.30
CaO .	0.52	0.33	0.45	0.15	0.17	0.25
Na_2O .	2.22	2.40	2.22	2.23	2.50	2.33
H_2O .	3.48	3.48	3.57	3.59	3.56	2.66
	100.00	100.00	100.00	100.00	100.00	100.00

Here, again, the agreements between analysis and theory are as close as could be reasonably expected. The same thing is true of the black tourmalines from Haddam Neck, Connecticut, and Nantic Gulf. Using letters to represent the several molecules, as above, the Haddam mineral is sharply represented by $\text{A}_4\text{B}_1\text{D}_2$, and that from Nantic Gulf by $\text{A}_6\text{B}_7\text{C}_3\text{E}_1$. Here is the comparison:—

	Haddam Neck.			Nantic Gulf.		
	Found.	Reduced.	Calc.	Found.	Reduced.	Calc.
SiO_2 ..	34.95	33.78	33.67	35.34	33.34	33.60
B_2O_3 ..	9.92	9.60	9.82	10.45	9.86	9.80
TiO_2 ..	0.57	—	—	0.40	—	—
Al_2O_3 .	31.11	30.74	30.67	30.49	29.01	28.84
Fe_2O_3 .	0.50	—	—	—	—	—
FeO ..	11.87	19.31	19.24	8.22	20.46	20.55
MnO ..	0.09	—	—	trace	—	—
MgO ..	4.45	—	—	7.76	—	—
CaO ..	0.81	0.78	0.75	2.32	2.19	2.15
Na_2O .	2.22	2.30	2.48	1.76	1.74	1.70
K_2O .	0.24	—	—	0.15	—	—
H_2O ..	3.62	3.49	3.37	3.60	3.40	3.36
	100.35	100.00	100.00	100.49	100.00	100.00

To the lithia tourmalines, as analysed by Riggs, a similar set of formulæ apply, although the comparison between fact and theory is not quite so close as in the preceding cases. The red tourmalines from Brazil and from Rumford, Maine, are very nearly represented by the expression—



with Li: Na approximately as 5:4. The slight deficiency in the alkalis is made up by the presence of small amounts of calcium, iron, and manganese, but the ratio $\text{Al}_8:\text{Si}_6$ is very clear. The green tourmalines are all lower in alumina, and range downward toward the iron end of the series; and like the latter are representable as mixtures of the following molecular types:—

* Bulletin of the United States Geological Survey, No. 167.

- A. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3(\text{AlOH}).\text{Fe}_4\text{H}_4$.
 B. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Ca}.\text{Fe}_4\text{H}_4$.
 C. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Li}.\text{H}.\text{Al}_2\text{Li}_2\text{H}_4$.
 D. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{NaH}.\text{A}_3\text{NaH}_2$.
 E. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{H}_2.\text{Al}_3\text{NaH}_2$.

Thus, the dark opaque green tourmaline from Rumford, Maine, is a molecular mixture corresponding to $\text{AgB}_2\text{C}_7\text{D}_{14}\text{E}_5$; the similar mineral from Auburn is $\text{A}_5\text{B}_1\text{C}_8\text{D}_{17}$; the light green from Auburn $\text{A}_2\text{C}_3\text{B}_{10}\text{D}_8\text{E}_{12}$, and the nearly colourless from Auburn, $\text{A}_1\text{B}_5\text{C}_{20}\text{D}_{10}\text{E}_{35}$. From Brazil the dark green is $\text{A}_2\text{B}_1\text{C}_6\text{D}_8$, and the light green is $\text{A}_1\text{B}_2\text{C}_9\text{D}_8\text{E}_5$. The complexity of these expressions is only apparent, not real, as a study of the original type formulæ will show. They compare with the reduced analyses as follows:—

	Rumford.		Auburn, dark.		Auburn, medium.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
SiO_2	36.68	36.69	36.37	36.45	37.95	37.52
B_2O_3	10.26	10.69	9.98	10.63	10.57	10.94
Al_2O_3	38.26	37.74	36.89	37.21	38.11	39.02
FeO	6.78	6.90	7.94	7.72	4.47	4.28
CaO	0.34	0.34	0.17	0.16	0.50	0.50
Na_2O	3.12	3.07	3.19	3.14	2.58	2.58
Li_2O	0.95	0.94	1.06	1.07	1.35	1.35
H_2O	3.61	3.63	4.40	3.62	4.47	3.81
	100.00	100.00	100.00	100.00	100.00	100.00
	Auburn, pale.		Brazil, dark.		Brazil, light.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
SiO_2	38.25	37.92	37.24	37.14	37.49	37.64
B_2O_3	10.30	11.05	9.95	10.83	10.32	10.97
Al_2O_3	39.92	40.17	38.66	38.07	39.86	39.04
FeO	2.75	2.56	5.49	5.24	3.74	3.61
CaO	0.43	0.49	0.30	0.35	0.49	0.46
Na_2O	2.55	2.53	2.90	3.01	2.59	2.76
Li_2O	1.34	1.34	1.63	1.64	1.71	1.69
H_2O	4.46	3.94	3.74	3.72	3.80	3.83
	100.00	100.00	100.00	100.00	100.00	100.00

(To be continued).

ON TRIVALENT CARBON.

(THIRD PAPER).*

By M. GOMBERG.

(Concluded from p. 21).

Compound of the Unsaturated Hydrocarbon with Acetic Ether.

A REACTION entirely analogous to the one described above takes place when acetic ether is substituted for absolute ether. A compound of the unsaturated hydrocarbon with acetic ether is at once formed when triphenylchloromethane, dissolved in the ester, is treated with zinc. It also produced when the metal is allowed to act upon the halogen compound dissolved in benzene, and to the concentrated solution acetic ether is added. The sample which furnished the results given below was prepared by the second method; it was washed fifteen times with acetic ester, and was thoroughly dried in an atmosphere of carbon dioxide.

0.3160 grm. substance gave 1.0180 grm. carbon dioxide and 0.2080 grm. water.

	Calculated for	Found.
Carbon ..	$2(\text{C}_6\text{H}_5)_3\text{C} + \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$.	87.86
Hydrogen ..		7.37

* From the *Journ. Am. Chem. Soc.*, xxiii, No. 7. The first paper appeared in the *Journ. Am. Chem. Soc.*, xxii, 757; the second in *Am. Chem. Journ.*, xxv, 320.

The compound of the hydrocarbon with the ester is perfectly colourless when first prepared, but soon turns pale yellow. It is more stable than the corresponding ether compound, and can be kept much longer without discolouration. It can be obtained in large crystals, or in the form of a granular crystalline powder. On heating, it loses the ester.

1.1170 grms. substance lost at 100° C. 0.1575 grm.

	Calculated for	Found.
Loss ..	$2(\text{C}_6\text{H}_5)_3\text{C} + \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$.	14.10
	15.50	

The escaping acetic ester was condensed and identified as such. The residue, after driving off the ester, looked like that obtained from the ether compound. It was amorphous, yellow, soluble in benzene and in carbon disulphide; it absorbed iodine, and gave the peroxide. An analysis gave the following results:—

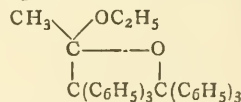
0.2135 grm. substance gave 0.7250 grm. carbon dioxide and 0.1322 grm. water.

	Calculated for	Found.
Carbon ..	$(\text{C}_6\text{H}_5)_3\text{C}$.	92.61
Hydrogen ..		6.93
	93.76	
	6.24	

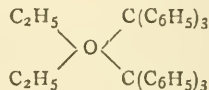
It will be noticed that in both instances the per cent of carbon is somewhat low for triphenylmethyl. This may be accounted for by a slight oxidation, but I have no explanation at present as to the cause of the rather high per cent of hydrogen.

What is the Nature of these Compounds?

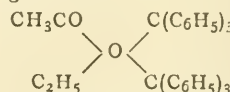
It is impossible to tell at this time whether in these two instances the ether and the acetic ester are those of crystallisation or of constitution. Such a distinction is at best but an arbitrary one. One would expect that ether of crystallisation would be easily driven off *in vacuo* over sulphuric acid—which is not the case in this instance. From the extreme unsaturation of the hydrocarbon it may be assumed that it might add itself to acetic ester, giving a body something like this:—



But it could hardly be expected that mere heating at 80—100° C. would break up a chain of three carbon atoms in such a way as to regenerate the ester. Then, again, the combination with ethyl ether precludes any such addition theory in that instance. If it is not ether of crystallisation, then the following constitution of that body suggests itself:—



and the acetic ester compound may be supposed to have the corresponding constitution:—



In support of such a constitution might be cited the remarkable avidity of the hydrocarbon for oxygen, and the possibility of oxygen to act as tetravalent. Such a possibility was foreshadowed by van't Hoff as long ago as 1877 ("Ansichten über die Organische Chemie"). There has since been accumulating a considerable amount of evidence of physical nature pointing to such a possibility. In connection with this may be mentioned the recent work of Kanonnikow. From a study of alcohols and ethers at their critical condition, Kanonnikow (*Journ. Russ. Phys. Chem. Soc.*, xxxiii, 197) comes to the conclusion that in

these compounds, under these conditions, the oxygen behaves as if it were tetravalent. The extreme unsaturation of triphenylmethyl presents an excellent opportunity to test the theory of the tetravalence of oxygen. The above formulæ for the two compounds must be looked upon, at present, as a mere suggestion. It is my intention to extend this study to other oxygen compounds, as well as to nitrogen derivatives, and I beg to reserve this field for further work.

ON PYRITE AND MARCASITE.*

By H. N. STOKES.

THE object of this paper is to describe a chemical method by which the native forms of iron disulphide may be distinguished with certainty, and by which their relative amounts in mixtures of the two may be quantitatively determined. The method is applied to various supposed pyrites and marcasites, and it is shown that in the absence of well-marked crystallographic features it is extremely easy even for experts to be deceived as to the nature of a given specimen.

I. UNCERTAINTY OF METHODS OF DISTINGUISHING PYRITE AND MARCASITE.

Pyrite and marcasite are usually distinguished by their differences of crystalline form, colour, density, and ease of oxidation.

Crystalline Form.

Pyrite usually crystallises in cubes, often in pentagon-dodecahedrons or octahedrons, and frequently in combinations of these and more complicated forms of the isometric system, while marcasite assumes various forms of the orthorhombic system. This criterion is inapplicable when the minerals assume the massive or compact form, or when they occur as concretionary nodules in which the crystalline form can not be made out. Moreover, pseudomorphs are not uncommon, and paramorphs of pyrite after marcasite and of marcasite after pyrite are said to occur, in which events no conclusion can be drawn from this source.

Colour.

The colour of pyrite is generally said to be pale brass yellow, while that of marcasite is described as tin-white, greyish white, greenish, brass-yellow, bronze-yellow, and in other terms. Dana† describes marcasite as pale bronze-yellow. These discrepancies are doubtless due to tarnished specimens having been described. Marcasite frequently assumes a yellowish tarnish, which may vary to copper coloured. On fresh surfaces, such as are obtained by breaking or by removing the film by warming with dilute hydrochloric acid, the colour is unquestionably tin-white or greyish white, closely matching platinum, and without a trace of yellow. The white colour is not an indication of the presence of arsenic (see *prox.*), as it is equally shown by specimens which are free from arsenic. To distinguish pyrite and marcasite by the colour, they must be cleaned with hydrochloric acid, and immediately examined under a good white light in comparison with standard specimens also freshly cleaned. The faint yellow of pyrite makes it extraordinarily easy to deceive oneself if the light be yellowish in tint. The differences of the supposed yellow and light-coloured pyrites vanish, except in rare cases, when these precautions are observed, and pyrite can usually be distinguished with ease when mixed with marcasite. In the case of fine-grained concretions, or where the surface is too rough to afford a good reflection, it is sometimes quite impossible to draw any conclusion from the colour.

Density.

Density according to Different Authorities.—The density of both minerals is subject to some variation, as shown by the following figures from different sources.—

Density of Marcasite and Pyrite.

Authority.	Marcasite.	Pyrite.
Dana (a)	4.85–4.90	4.95–5.10
Rammelsberg (b) ..	4.90	5.00
Julien (c)	4.80	5.01
Stokes (d)	4.88–4.90	5.02–5.04

(a) "System of Mineralogy," 6th Ed., Pp. 85, 94.

(b) *Zeit. Deutsch. Geol. Gesell.*, 1864, vol. xvi., p. 267. Supposed normal density.

(c) *Annals New York Acad. Sci.*, 1887, vol. iv., pp. 177, 210. Supposed normal density.

(d) See "Data for Pyrites" (*prox.*).

Density not a sure Criterion of Composition.—My own determinations were made with the pycnometer at 18–23°, on the purest obtainable material, coarsely powdered. Julien's figure for marcasite is certainly too low. The following list, giving the densities of some specimens of which I have determined the composition (after deducting impurities), shows how illusive may be conclusions as to the relative amounts of pyrite and marcasite based on density alone:—

Densities of some Specimens of Pyrite and Marcasite.

No. of specimen.	Density.	Composition, chemically determined.
5.	5.041	100 per cent pyrite.
3.	5.023	100 per cent pyrite.
33.	4.987	83.5 per cent pyrite, 16.5 per cent marcasite.
7.	4.891	100 per cent marcasite.
10.	4.886	100 per cent marcasite.
12.	4.880	100 per cent marcasite.
29.	4.856	99.5 per cent pyrite.
30.	4.843	99.5 per cent pyrite.
31.	4.819	100 per cent pyrite.
17.	4.563	100 per cent pyrite.

Oxidation.

While it is unquestionably true that marcasite oxidises more rapidly than pyrite under the same conditions, a compact, well-crystallised marcasite can be kept almost indefinitely without any change further than a superficial tarnish, whereas finely divided or porous pyrite oxidises with great rapidity, and this fact has frequently caused pyrite to be mistaken for marcasite.

The amount of oxidation depends upon the time during which the specimen has been exposed; upon the peculiar conditions under which it has occurred, such as exposure to dry or moist air, or to water holding oxygen or other oxidising agents in solution; upon whether the oxidation products are removed; upon the surface exposed per unit of volume; and upon an oxidation factor characteristic of each mineral, but probably not more than three times greater for marcasite than for pyrite. It is obvious, therefore, that no trustworthy conclusion can be drawn in any case from vitriolisation in the absence of definite knowledge of these factors; and even when the conditions of time and exposure are identical, as when the specimens are kept side by side in the cabinet, it is necessary to know the $\frac{\text{surface}}{\text{mass}}$ factor before rapid vitriol-

isation justifies one in pronouncing a specimen to be marcasite. One of the most extreme cases of rapid vitriolisation that I have seen is No. 21 (see *prox.*, "Quantitative Composition of Specimens of Doubtful Nature"), which consists of nodules of practically pure pyrite. Many of the rapidly vitriolising specimens consist of mixtures of pyrite and marcasite, and apart from the porosity existing in such cases it is possible that an electrochemical

* From the *Bulletin of the U.S. Geological Survey*, No. 186.

† "System of Mineralogy," 6th ed., p. 94; for a list of terms and references see Julien, *Annals New York Acad. Sci.*, 1887, vol. iv., p. 179.

action between the two may assist the oxidation. It is hardly necessary to add that the old idea that marcasite tends to produce ferrous sulphate, and pyrite to give limonite, is untenable.

Penfield's Method.

Penfield (Brush and Penfield, "Determinative Mineralogy," 15th Ed., p. 252) has described a method of distinguishing the two minerals, based on treating the finely powdered substance with strong nitric acid under identical conditions; pyrite dissolves completely, while marcasite leaves a residue of sulphur. While this procedure serves well to distinguish the pure minerals, it is obviously incompetent to detect pyrite in the presence of marcasite.

Action of Copper Sulphate on Pyrite and Marcasite.

A. P. Brown (*Proc. Amer. Philos. Soc.*, 1894, vol. xxxiii., p. 225; *CHEMICAL NEWS*, 1895, vol. lxxi., p. 179) asserts that when marcasite is heated for six hours at 200° with 10 per cent copper sulphate solution its iron is completely dissolved as ferrous sulphate, while under the same conditions pyrite yields a mixture of 2 mols. ferric and 1 mol. ferrous sulphate; and on this he bases the conclusion that in marcasite the iron is wholly in the ferrous condition, $\text{Fe}''\text{S}_2$, while in pyrite it is four-fifths ferric, $\text{Fe}''\text{S}_2(\text{Fe}'''\text{S}_2)_4$. As Brown's work might seem to afford a means of distinguishing the two minerals, and as the different constitution, if existing, would have an important bearing on the question of their formation in nature, I have repeated these experiments, but with totally different results. The details of my experiments are given further on, and I here state merely my conclusion that the only recognisable difference is the greater ease with which marcasite is attacked by the cupric solution, and that no evidence can be obtained in this way as to any difference of chemical constitution.

II. BEHAVIOUR OF PYRITE AND MARCASITE TOWARD FERRIC SOLUTIONS.

In the course of an investigation on the action of ferric salts on natural sulphides, differences observed in the behaviour of pyrite and of marcasite were so marked as to make it seem probable that on these differences there might be based a method of distinguishing these minerals, and of determining them quantitatively in mixtures, thus establishing a sure means of ascertaining the composition of concretions and other doubtful specimens, and of testing the validity of the conclusion of Julien, quoted below (see *prox.*), that many supposedly pure pyrites and marcasites are mixtures of the two. While approximate results were soon reached, many fruitless experiments had to be made before all important sources of error were eliminated, and before the process could be brought to a reasonably satisfactory quantitative basis. Only the results obtained by the perfected method are presented in this paper.

Action of Ferric Chloride.

It has long been known that ferric salts attack pyrite. L. L. de Koninck (*Annales Soc. Geol. Belgique*, 1883, vol. x., p. 101; *Zeit. Anorg. Chemie*, 1901, vol. xxvi., p. 123) found that pyrite is oxidised at 170–200° C. by ferric chloride or ferric ammonium alum, with formation of a ferrous salt and sulphuric acid. J. H. L. Vogt (*Trans. Amer. Inst. Min. Eng.*, Richmond Meeting, February, 1901) mentions that pyrite is very slowly attacked in the cold by 30 per cent ferric chloride solution, giving a trace of sulphuric acid. He regards the formation of sulphuric acid as subordinate, and does not ascribe an important rôle to ferric salts in the decomposition of pyrite. Julien (*Annals New York Acad. Sci.*, 1887, vol. iv., p. 138–139) observed a reduction of ferric chloride by marcasite. No quantitative study of these reactions has been made, so far as I can ascertain.

Percentage of Sulphur Oxidised.

Preliminary experiments showed that very little dilute

solutions of ferric salts attack pyrite rapidly at the boiling temperature, and much more slowly, but quite appreciably, in the cold. It is upon the determination of the percentage of sulphur oxidised in the total mineral decomposed that the new method is based. If ferric chloride be used, the amount of mineral decomposed can be found from the increment of iron in the solution, and the SO_4 determined as barium sulphate. An experiment with a ferric chloride solution containing 1.14 grms. Fe''' per litre, with a little hydrochloric acid, which was boiled to complete reduction with an excess of powdered pyrite free from sulphate, in a current of carbon dioxide, showed that 65 per cent of the sulphur was oxidised, a result agreeing well with the results presented below.

(To be continued).

NOTICES OF BOOKS.

Studies from the Chemical Laboratory of the Sheffield Scientific School. Edited by HORACE L. WELLS. New York: Charles Scribner's Sons. London: Edward Arnold. 1901. 2 vols. 8vo. Pp. 379 and 444.

THE half-title page preceding the one given above bears the additional words: "Yale Bi-Centennial Publications"; and a note states that these volumes form part of a series prepared by the Professors and Instructors with the approval of the President and Fellows of Yale University, issued in connection with the Bi-Centennial Anniversary (held in the autumn of 1901), as a partial indication of the character of the studies in which the University teachers are engaged.

These sumptuously made and carefully edited volumes show what the Sheffield Chemical Laboratory has done and is doing in the way of scientific research, and the papers here reprinted from periodicals are limited to the work done by the present officials chiefly during the last ten years. These restrictions as to persons and time prevent the "studies" from giving an adequate conception of the vast amount of first-class investigations in chemistry that have been issued from the department of Yale University, of which the Sheffield Scientific School is so prominent a member. At the same time, these limitations enable the authorities to show to the public the activity of the present teaching forces, which comprise no less than eight professors and instructors in divers branches of chemistry.

No review of the researches contained in these volumes could be made satisfactory without some notice of the institution itself. The chemical department of the school was the earliest established; it was first conducted in what had been the "President's House," but in 1860, through the liberality of Joseph E. Sheffield, it was united to an Engineering Department (already in operation), and removed to Sheffield Hall, in which new and commodious laboratories were then constructed; there it remained for thirty-five years. The teaching force was gradually increased, a wider range of instruction was introduced, and the names of certain gentlemen associated with the school became widely known; notably, George J. Brush, the mineralogist; Samuel W. Jonson, the authority on agricultural chemistry; O. D. Allen, who had charge of analytical chemistry and metallurgy; and W. G. Mixer and Russell H. Chittenden, whose researches in physiological chemistry are renowned.

The first volume is devoted to papers on general inorganic chemistry and on double halogen salts; they are all reprints of articles that have appeared in the *American Journal of Science*, the *American Chemical Journal*, and elsewhere, and embrace a great variety of topics. "Cæsium Trihalides" form the subject of the first paper, by the editor of the volumes; then follow several other articles embodying further researches

on caesium salts by the same author and his associates. Also one on the purification of caesium material, for this rare element has herein received much attention. Other papers are on special analytical methods, on an isomer of potassium ferricyanide, on trivalent vanadium, &c.; only one dealing with points in pure theory, the Periodic System, by James Locke.

In the second half of Volume I. are papers on the double halides of several elements, among which caesium and its comrades are prominent.

Volume II. contains numerous papers on organic chemistry, to which the name of Professor H. L. Wheeler is most frequently attached. Among them may be named those bearing the following titles;—"Researches on the Iso-Anilides," "On Diacid Anilides" (several papers), "Researches on the Cyclo-amidines, and on the Cyclo-Amides," "On the Re-arrangement of Imido-Esters," &c., all being contributions to knowledge of high rank.

Accompanying these is a bibliography of the principal publications of the present officers of the Sheffield Scientific School, so far as the work has been done in New Haven.

The "Studies" reflect great credit on their authors and on the institution whence they spring; the series of volumes of which these form a part make a notable exhibit of the activity of the famous Yale University. H.C.B.

Chemistry and Physics; a Manual for Students and Practitioners. By WALTON MARTIN, Ph.B., M.D., and WILLIAM H. ROCKWELL, Jun., M.D. Series edited by BERN B. GALAUDET, M.D. Illustrated with 137 Engravings. London: Henry Kimpton. 1901. Pp. 374.

THOUGH not very clearly stated in the title, we gather that this book is intended specially for medical students and practitioners, to whom a knowledge of chemistry and physics is important. The authors have endeavoured as far as possible not to give undue prominence to the medical aspect of certain chemicals which are also drugs, nor to certain uses of electricity which are employed in the treatment of disease, as they feared to encroach upon *Materia Medica* and *Electro-therapeutics*. At the same time, those compounds, especially in the section of organic chemistry which are of medical interest, have received more detailed descriptions than those which are of interest only to the chemist pure and simple. The book is well and clearly printed and bound, and is furnished with a very complete index.

Die Normalelemente und ihre Anwendung in der Elektrischen Messtechnik. By Dr. W. JAEGER. Halle-a-S.: Wilhelm Knapp. 1902.

THE recent developments in the theory of normal elements are dealt with at considerable length and with conspicuous clearness in this book. The Latimer Clark cell and its various modifications are dwelt upon very minutely both from a theoretical and practical point of view. In the section on theory Cohen's latest work on the thermodynamics of the normal element is well summarised, and in all respects the book seems comprehensive and well up-to-date.

Beiträge zur Chemischen Physiologie und Pathologie. I. Band. Hefte 1—4. Braunschweig: Friedrich Viewig und Sohn. 1901.

THIS new periodical, which is to be issued at short intervals under the editorship of Dr. Franz Hofmeister, is intended to meet the demand for a journal of biochemistry, occupying itself with pathology and physiology regarded from a chemical point of view, and treated by chemical methods. Judging from these two first issues, which contain much interesting matter communicated by well-known physiological chemists, the new publication seems likely to prove useful in extending our knowledge of the chemistry of the animal organs, secretions, &c.

Special mention must be made of the reports of Dr. Leo Langstein's work on ovoglobulin and ovalbumin, and of Dr. H. Conradi's paper on the coagulation of the blood.

Roscoe-Schorlemmer's Ausführliches Lehrbuch der Chemie. By J. W. BRÜHL. *Organische Chemie.* Teil VII. Braunschweig: Friedrich Viewig und Sohn, 1901.

THIS volume brings to an end the complete revised edition of Roscoe and Schorlemmer's "Text-book of Chemistry," and includes the systematic and alphabetical indexes of the whole work so that they may be readily detached and bound separately.

The albuminous substances form the subject of the first and greater part of the book; following Hammarsten's classification, they are dealt with under the headings, (1) products derived from true albumens including albuminates, (2) true albumens, (3) proteids, and (4) albumenoids. The rest of the book is occupied with the bile substances, enzymes, and ptomaines; in the case of this last section, and indeed throughout the whole volume, much of the material has been collected from original papers and brought together for the first time in the form of a text-book, many of the researches described being of quite recent date.

This last volume fully maintains the high level of excellence reached in the previous volumes both in matter and arrangement, and it is much to be regretted that no English translation of the whole text-book is to be obtained. The world of science owes a debt of gratitude to those who produce a treatise such as this, embracing the whole range of pure chemistry, no less than to those who discover or enquire into new developments of the science.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 25, December 16, 1901.

This number contains no matter of chemical interest.

No. 26, December 23, 1901.

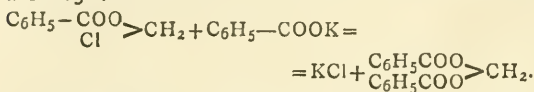
Dilution Constants of Saline Solutions.—Albert Colson.—The author experiments on the relation between the degree of dilution of a saline solution and the heat of solution. Solutions of NaCl, KCl, NaNO₃, and KNO₃ were tried, and a table of numbers is given.

Metallic Strontium and its Hydride.—M. Guntz.—The author obtained a considerable quantity of strontium by the electrolysis of an aqueous solution of its chloride, using a cathode of mercury. An amalgam is formed from which the strontium can be obtained by slow heating in a vacuum in an iron crucible, the mercury gradually distilling off. The properties of strontium are similar to those of barium. Strontium seems, however, to combine less easily with liquid ammonia.

Two Blue Oxides of Molybdenum.—G. Bailhache.—In a preceding paper the author described the preparation of blue oxide of molybdenum from the compound Mo₂O₅.2SO₃. A concentrated solution of Mo₂O₅.2SO₃ when exposed to the air gradually changes from brown to green, and finally to blue. At the same time a blue substance is deposited at the bottom of the vessel. The composition of this latter body is very variable. The blue solution when treated with ammonium chloride precipitates a blue oxide, but its purification is very difficult. The author now proves that this variation in composition is due to the formation of two oxides of molybdenum,

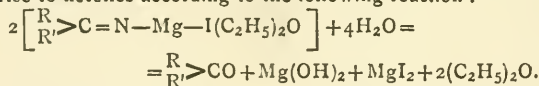
both blue in colour. These are obtained separately from BaMoO_4 , and have the respective formulæ $\text{Mo}_2\text{O}_3 \cdot 2\text{MoO}_4 \cdot 6\text{H}_2\text{O}$ and $(\text{Mo}_2\text{O}_3)_3(\text{Mo}_7\text{O}_{24})_2 \cdot 18\text{H}_2\text{O}$. These two oxides present absolutely the same characteristics. The only reaction by which they may be distinguished is their action on alkalis; a slightly different coloured precipitate is formed in the two cases. The author intends to further investigate this matter.

Chlorobenzoate and Dibenzoate of Methylene.—Marcel Descudé.—Chlorobenzoate and dibenzoate of methylene may be obtained simultaneously and in nearly equal proportions by the action of benzoyl chloride on trioxymethylene in presence of zinc chloride. The chlorobenzoate is a colourless liquid, heavier than water (sp. gr. = 1.236), in which it is insoluble. It solidifies at -15° , and is very highly refracting. It can be transformed quantitatively into the dibenzoate by heating equivalent weights of the chlorobenzoate and dry potassium benzoate for about four hours at a temperature of about 150° .



Hyposulphites of Aromatic Amines.—A. Wahl.—When a solution of sodium hyposulphite is added to a solution of aniline chlorohydrate, a voluminous crystalline precipitate is formed. These crystals, when re-dissolved in water at $30-40^\circ$, deposit on cooling, and when thus purified possess the composition of aniline hyposulphite $(\text{C}_6\text{H}_5\text{NH}_2)_2 \cdot \text{H}_2\text{S}_2\text{O}_3$. All the primary amines which the author examined, both in the benzenic series and in the naphthalenic series (aniline, ortho-, meta-, and paratoluidine, α - and β -naphthylamine), give normal hyposulphites corresponding to the formula $(\text{RNH}_2)_2 \cdot \text{H}_2\text{S}_2\text{O}_3$. The secondary and tertiary amines do not give the corresponding hyposulphites.

New Reactions of Organometallic Derivatives (IV.). Synthesis of Ketones.—E. E. Blaise.—In a preceding paper the author showed that the ethero-organomagnesium derivatives react on the nitriles, and give in certain cases easily isolated crystalline compounds. These compounds are instantly decomposed by water, and give rise to ketones according to the following reaction:—

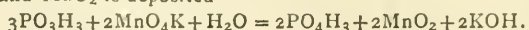


This reaction is very general. It takes place in the cyclic series as in the fatty series, but the best yields are obtained with alcoholic iodides and cyclic nitriles.

Basic Properties and Tetravalence of Oxygen in the Xanthene Series.—R. Fosse.—The author first establishes the fact that the mono-halogenated derivatives of the xanthene series possess basic properties. He also shows that such bodies obtained either by the action of the halogens on the xanthenes or by the hydracids on the corresponding hydrols, behave in the same manner as amine salts by forming compounds with many reactions of alkaloids, &c.; in fact, the compounds formed seemed to behave like hypochlorites of these bases.

MISCELLANEOUS.

A Volumetric Method for the Estimation of Phosphorous Acid.—O. Kühling.—The solution is first oxidised with warm permanganate; it becomes alkaline and MnO_2 is deposited—



In order to get a good deposit of MnO_2 it is advisable to add sulphate of zinc, which reacts on the potash. The

following are the details of the method. The liquid containing from 0.32 to 0.7 gram of PO_3H_3 in 20 or 40 c.c. is poured into an Erlenmeyer flask of 250 c.c. capacity, treated with 20 to 40 c.c. of a 10 per cent solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, then with a not quite sufficient quantity of KMnO_4 , heated on the water-bath until the colour disappears, then again treated with more KMnO_4 , heated again, and finally treated with the small amount of KMnO_4 which is absolutely necessary for the colouration to persist after heating for fifteen minutes. The solution is filtered again and an excess of KMnO_4 added, then heated on the water-bath with frequent stirring; on cooling it is diluted with an equal volume of water, and the precipitated MnO_2 collected on an asbestos filter, and after careful washing it is placed in a flask and treated with an acidulated solution of potassic iodide. The oxide is dissolved in the cold by the help of frequent shaking; this sets free the iodine which is titrated by hyposulphite. As an alternative the excess of KMnO_4 in the filtrate can be determined direct.—*Berichte*, vol. xxxiii., p. 2914.

Action of Peroxide of Hydrogen on the Hyposulphites.—A. Nabl.—On adding together equimolecular portions of peroxide of hydrogen free from H_2SO_4 and a solution of hyposulphite of soda, the author could not detect the formation of a hydrosulphite as announced by M.M. Bernthsen and Bazlen, but he observed that the liquid became sensibly warmer and took an alkaline reaction. Equal molecules of sulphate and sulphite of sodium were formed, as well as a basic substance oxidisable by an excess of H_2O_2 and not very stable, as the liquid when left to itself soon becomes cloudy and gives off SH_2 . An attempt was made to isolate this sulphurised base by acidulating with hydrochloric acid after the action of the H_2O_2 was completed, then evaporating to dryness on the water-bath, taking up with water, filtering, and precipitating with HgCl_2 . A partial reduction of the salt takes place; the base gives a double mercurous-mercuric salt, which, after washing, was treated with SH_2 . The filtered solution was evaporated almost to dryness on the water-bath, and, on the addition of alcohol and dilute sulphuric acid, a fine flocculent white precipitate of a sulphate was formed. This last salt was collected on a filter, washed with etherised alcohol, re-dissolved in water, then treated with carbonate of baryta, when it gave a colourless liquid with a green fluorescence and having a strongly alkaline reaction; the return is not good. This substance precipitates the metallic oxides from their saline solutions, reduces Fehling's solution slowly when warmed, and with SnCl_4 gives stannous sulphide. Its chloroplatinate becomes reduced slowly and spontaneously in the cold, but rapidly when warmed. It is probable that this base contains the radical SOH and can be compared with Cahours' hydrate of trimethylsulphine, or again with hydroxylamine.—*Berichte*, vol. xxxiii., p. 3093.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Society of Arts, 8. (Cantor Lectures). "The Purification and Sterilisation of Water," by Samuel Rideal, D.Sc., F.I.C.
- TUESDAY, 21st.—Royal Institution, 3. "The Cell—its means of Offence and Defence—Immunity," by Allen Macfadyen, M.D., B.Sc.
- Society of Arts, 8. "The Architect's Use of Enamelled Tiles," by Halsey Ricardo.
- WEDNESDAY, 22nd.—Society of Arts, 8. "Scientific Observations at High Altitudes," by Rev. J. M. Bacon.
- THURSDAY, 23rd.—Royal Institution, 3. "Recent Excavations at Delphi and in the Greek Islands," by A. S. Murray, LL.D., F.S.A.
- Society of Arts, 4.30. "Bengal—The Land and its People," by F. H. Skrine.
- FRIDAY, 24th.—Royal Institution, 9. "The Discovery of the Future," by H. G. Wells, B.Sc.
- Physical, 5. "The Factors of Heat," by James Swinburne. Exhibition of some Twinned Crystals of Selenite, by Eustace Large.
- SATURDAY, 25th.—Royal Institution, 3. "Landmarks in the History of Opera" (with Musical Illustrations), by W. H. Hadow, M.A., Mus.Bac.

THE CHEMICAL NEWS.

VOL. LXXXV., No. 2200.

RESEARCHES ON THE PRESSURE FORCES OF LIGHT.

By PETER LEBEDEV.

In the exposition of his electromagnetic theory of light, Maxwell (1873) took into consideration those forces which appear as forces capable of doing work ("weight moving") in an electrically or magnetically polarised medium. As a necessary consequence of his theory it follows that these forces must appear in a pencil of rays, and Maxwell says:—

"In a medium in which an undulation is propagated a pressure acts in the direction of propagation, and this pressure is at every spot numerically as great as the energy referred to unit volume at that spot."

Heaviside, Lorentz, Cohn, and Goldhammer have recently more closely investigated Maxwell's deduction concerning the existence of such pressure forces.

In quite a different way, and apparently without knowing of Maxwell's result, Bartoli (1876) arrived at the same conclusion; he describes a series of processes by which it is said to be possible to transfer by means of movable mirrors the radiating energy from a colder to a warmer body, and calculates the work to be done according to the second main proposition. The necessity for the performance of work in moving the mirror in the direction opposite to that of the incident ray forces us to the assumption of pressure forces which are exerted by this ray on the mirror. Bartoli calculated the magnitude of these pressure forces; his result agrees perfectly with that obtained by Maxwell.

The method employed by Bartoli was followed by Boltzmann, and afterwards by Prince Galitzin and Guillaume in calculating the pressure forces which are exercised by the ray; Drude extended this method to absolutely black bodies.

If a beam of parallel rays falls normally on a plane surface, the magnitude of this pressure of Maxwell and Bartoli, p , is determined if the quantity of energy per unit of time, E , the reflecting power of the surface, ρ , and the velocity of transmission of the ray, V , are known. We then have—

$$p = \frac{E}{V}(1 + \rho);$$

where ρ lies between 0 for an absolutely black substance and 1 for a perfectly reflecting substance.

These pressure forces are very small. Maxwell as well as Bartoli has calculated that the rays of the sun falling normally on 1 sq. c.m. exert a pressure which amounts to 0.4 m.grm. for an absolutely black surface, and 0.8 m.grm. for a plane mirror.

Conjectures that such pressure forces of the rays must exist have been expressed long before this time. So Kepler (1619) believed that the explanation of the force of repulsion which the sun exercises on comets' tails was to be sought for in the pressure forces of its rays, an idea which agreed with the prevailing emission theory of light, and which was ardently defended by Longomontanus. The same reason lead Euler (1746) also to ascribe pressure forces to the sun's rays, and he tried to establish the necessity for the existence of such forces on the movements of light considered as longitudinal vibrations.

De Mairan (1754) with Du Fay made very interesting attempts to prove these suppositions experimentally; but he soon perceived that the warming of the surrounding

air prevented any sure proof of the existence in light of forces capable of doing work. Considering the means at his disposal in the eighteenth century, De Mairan's experiments deserve the greatest admiration. A. Fresnel (1825) also made similar attempts, and likewise met with the same difficulties; an investigator of similar phenomena led Crookes to the discovery of the radiometer forces. The applications of which these pressure forces of Maxwell and Bartoli are capable, both in physics and astronomy, render an experimental investigation of them specially desirable, as both Maxwell and Bartoli's theoretical deductions rest upon certain simple properties of the absorbing and reflecting surfaces; and it would appear doubtful whether from these properties alone the forces capable of doing work could be determined for light rays also. A direct experiment leads most simply to this end.

Zöllner and Bartoli's efforts in this direction have led to no positive result; for this reason I undertook the following experimental research on the pressure forces of light:—

I. The Preliminary Experiments.

In his text-book Maxwell says:—"Concentrated electric light will probably exert a still greater pressure (than sun rays), and it is not impossible that the rays of such a light if they fell on a thin metallic leaf delicately suspended in a vacuum would produce an appreciable mechanical effect."

When I wished to begin my experiments the order of procedure proposed by Maxwell seemed to be hopeless, because already Zöllner had followed this method without result, and also "had observed that the value (of light pressure) obtained theoretically by Maxwell was about 100,000 times smaller than the value of the results observed by Crookes* in a special case." Even if one could reckon on appreciably diminishing these disturbing radiometer effects, I thought nevertheless, that only such contrivances by which these radiometer forces were compensated could give the desired result.

In research on the radiometer forces Schuster had proved that these forces are intrinsic forces of the radiometer. Righi proved this in an elegant way. He says:—"I let a radiometer float in water head downwards, so that the glass cap of the mill lay on the tube which kept the latter from falling out of the normal position by means of which a friction resulted, which stopped the revolution of the mill. When an intense beam of rays was directed on the mill, not the least revolution (of the radiometer) occurred." Bertin and Garbe obtained the same result on the repetition of this experiment.

I applied Righi's method of procedure to the determination of Maxwell and Bartoli's pressure forces of light as follows:—Between two circular covers stamped out of very thin nickel leaf a piece of mica was bent to the form of a cylinder, and securely fastened—consequently, a cylindrical radiometer body was formed—in which the vane was rigidly fastened to the covering. This radiometer was hung in an exhausted glass globe by a glass thread. When the light of an arc lamp was directed on the vane immediately revolution of the radiometer was observed,† the magnitude of which corresponded to Maxwell and Bartoli's pressure forces.

In the experiments when, for the sake of comparison, I investigated the effect on the radiometer vane by itself without the mica covering, I found that the radiometer forces which appeared were considerably smaller than those mentioned by Zöllner, and even produced an

* In his calculation Zöllner took the energy of total radiation of a candle too small. If we compare the radiometer forces observed by E. Nichols (*Wied. Ann.*, 1897, ix., p. 405) with the Maxwell and Bartoli press forces calculated from the radiation measurements of K. Angström (*Wied. Ann.*, 1899, lxvii, p. 647) we get a proportion of about 10,000.

† Righi, as well as Bertin and Garbe, observed no effect of the pressure forces of Maxwell and Bartoli in their experiments only because their methods intended for the detection of the very much greater radiometer forces were not sensitive enough for the forces of light.

essentially smaller disturbance, like the disturbances resulting on the proportionally great radiometer covering,

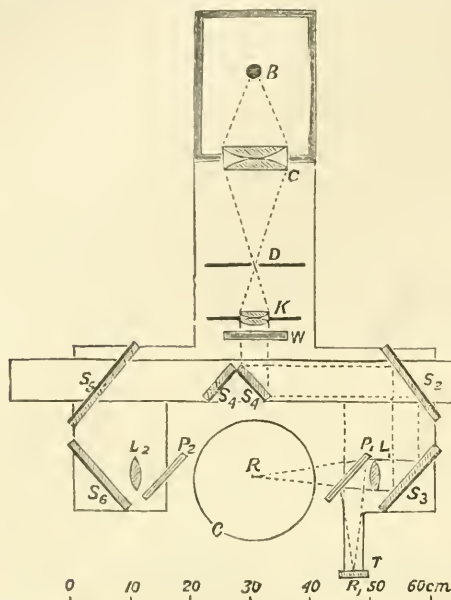


FIG. 1.

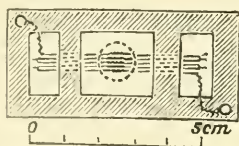


FIG. 2.

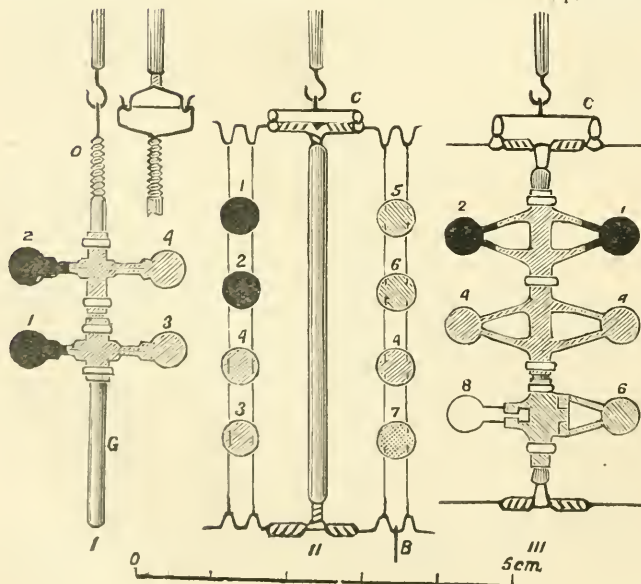


FIG. 3.

owing to convection. Therefore, I gave up this method, and undertook the research in the simple way proposed by Maxwell.

II. The Apparatus and Preparation of the Experiment.

Two difficulties are met with in carrying out research on Maxwell and Bartoli's pressure forces of light; the disturbances caused by convection and the radiometer forces which arise. By the greatest rarefaction these disturbing forces are diminished, but must, nevertheless, be taken into consideration in the measurements.

The disturbances by convection are due to the fact that on warming the vane by exposing it to the light the surrounding atmosphere is warmed also, and a slowly ascending current is caused. If the plane of the vane has even a small (almost negligible) inclination to the vertical plane, the rising current of gas exercises a force of torsion on the vane which is dependent *only* on the degree of warming, but *not* on the direction in which the heating rays fall. This disturbance can be eliminated by directing the beams from the same source, first on one side and then on the other side of the vane.

The disturbance by radiometer forces were reduced to a minimum by making the glass globe as large as possible, excluding by means of a ray-filter all rays which could be absorbed by the glass wall of the globe, making the vanes of thin metal leaf in order to equalise the distribution of heat, and, moreover, exhausting the globe as completely as possible by means of a mercury pump and the application of freezing mixtures.

If the radiometer forces are small, the corresponding correction can be calculated as follows:—The radiometer forces are directly proportional to the difference of temperature between the illuminated and dark surfaces of the vane, or for two vanes of the same material having their surfaces in the same state proportional to their thicknesses.* If we make simultaneous observations of *two* similar vanes of very different thicknesses we can calculate how far the light would cause the vane to turn, if the thickness of the vane were zero, and also the radiometer force zero. I must here remark that this correction is to be made only in the case of platinised vanes; for metal vanes the radiometer forces were, contrary to all expectation, indefinitely small.

* In our experiments the temperature difference between the illuminated vane and the globe was very much greater than the temperature difference between both surfaces of the vane. To whichever

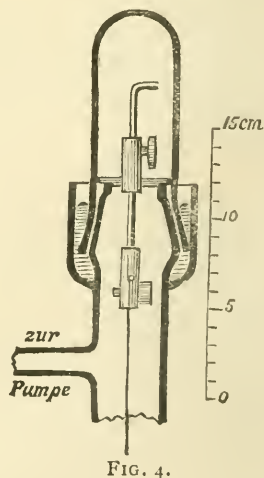


FIG. 4.

function of the first temperature difference the radiometer forces may be proportional, their "weight moving" effect on the vane shows their difference to both surfaces of the vane, and this is approximately directly proportional to the second temperature difference.

Besides the well known disturbing influences just mentioned another hypothesis must not remain unnoticed, namely, that the dispersion of light by illuminated surfaces, pointed out by Lenard and Wolf, could cause perceptible "weight moving" reaction forces, and these must always appear as an accompaniment of Maxwell and Bartoli's pressure forces of light; but these hypothetical reaction forces must be dependent on the colour of the incident light as well as on the chemical nature of the vane. Experiments with coloured light and with different vanes have not led to the discovery of any appreciable effects of these reaction forces.

The following arrangement was used:—The image of the terminal of a direct current arc lamp, B (30 ampères), was cast on a metal diaphragm, D ($d=4$ m.m.), by means of a condenser, C. The cone of light coming from the diaphragm was converted into a beam of parallel rays by the lens, K. In order to free the light from ultra-red rays, behind the lens, K, was a glass vessel filled with pure water,* parallel to the plane of the lens (thickness 1 c.m.); in the place of this a ruby-red glass could be used, the pure water being replaced by an ammoniacal solution of copper.†

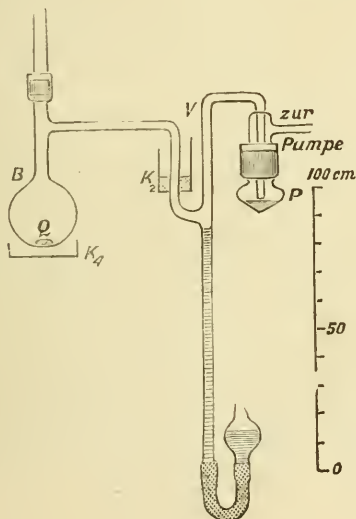


FIG. 5.

On its further passage the pencil of rays was reflected from the plane glass mirrors, S_1 , S_2 , and S_3 , situated in the rear, and then re-united by the lens L_1 to a real enlarged ($d'=10$ m.m.) image at R of the diaphragm D in the interior of the glass globe. If the pair of mirrors, S_1 and S_4 , were moved along, the rays would pass similarly, and fall on the vane suspended in the glass globe G from the other side. The lenses L_1 and L_2 had a focal length of 20 c.m., and a diameter of 5 c.m., so that the incident light has an aperture angle of about 15° .

The mirror apparatus was rigidly connected with the arc lamp. The lamp stood on a sliding base on which it could be turned towards or away from the glass globe. The cone of light could be raised or lowered by means of an adjusting screw.

The sudden fluctuations in the intensity of the light, which are unavoidable in the case of an arc lamp, can be rendered harmless only by making many observations.

In order to be able to reduce the separate series of measurements to a constant mean light-intensity, the fol-

lowing arrangement was used:—Between the lens L_1 (Fig. 1) and the glass globe G a thin plane glass plate, P_1 , is placed at an angle of 45° to the direction of the rays. The greater number of the rays pass through the glass plate without hindrance, while the reflected light combines to form a real image, R_1 , and this falls on the thermopile τ . The thermopile (Fig. 2) is composed of five Constantin iron elements (wire thickness, $d=0.025$ m.m.), which are mounted in an ebonite frame and closed with glass plates; the relative light-intensity is measured by the deflections of a d'Arsonval's galvanometer. In order to diminish similarly the light coming from the lens L_2 (Fig. 1), a corresponding glass plate, P_2 , is interpolated. The light-intensity can only be controlled if the two mirrors, S_1 , S_4 (Fig. 1), stand in the positions shown in the diagram. If they are moved, no light falls on the thermopile, and this position determines the galvanometer zero point.

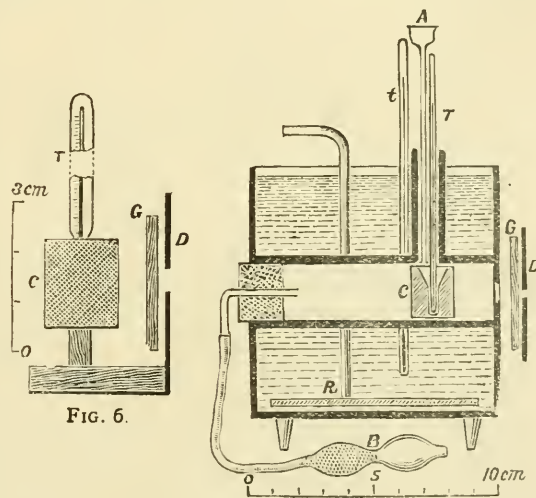


FIG. 6.

FIG. 7.

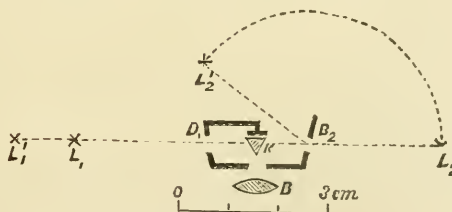


FIG. 8.

Three different kinds of vane apparatus were used (Fig. 3).

Vane apparatus I. consists of a glass rod, G, to which two cross-pieces made of platinum-leaf of different thicknesses were rigidly fixed by means of platinum wire rings (without cement); in order to make the circular discs (diameter 5 m.m.) of the same size, a steel stamp was used. Two of the discs were blank on both sides; two others platinised on both sides—the thicker five times more strongly than the thinner. To suspend the apparatus on the double hook of a torsion arrangement, a platinum loop, O, melted into the glass rod G was used; this was perpendicular to the direction of the vane arms, so that on suspension the glass rod G was free to move vertically in the plane of these arms.

Vane apparatus II. (Fig. 3, II.) consisted of a glass rod into which arms of platinum wire were melted. Between these platinum arms fine platinum wires (0.05 m.m.) were

* Thus all ultra-red rays with $\lambda > 1.2 \mu$ are excluded; glass lenses stop the ultra-violet rays.

† The available energy is reduced by the red and the blue ray filters to about one-fifth that of white light; that is a proof that the radiation employed belongs almost exclusively to the visible part.

stretched, which went through little holes in four metal discs, and held these firmly in a vertical position in the plane of the platinum arms; these platinum wires were so thin that their radiometer effect could be neglected. The vane apparatus was provided with a Cardani's suspension arrangement of platinum wire, *c*, and by means of this hung on the platinum hook of the torsion thread; the vertical position of the glass rod *g* was secured by means of an additional weight of platinum wire, *b*.

Vane apparatus III. was similarly constructed to I., and had a Cardani's suspension arrangement. The strips of tin plate which served as arms for the discs were very narrow (0.3 m.m.), and yet they satisfactorily ensured the vertical position of the discs.

The mica wing (8) was fastened in an aluminium setting. Aluminium arms were placed at the top and bottom to prevent the vanes striking against the glass wall of the neck of the globe while the apparatus was being suspended.

The following vanes were experimented with:—

No.	Material.
1.	Platinum, thickly platinised.
2.	" five times more thickly platinised.
3.	" blank. Thickness = 0.10 m.m.
4.	" " " = 0.02 "
5.	Aluminium, " " = 0.10 "
6.	" " " = 0.02 "
7.	Nickel, " " = 0.02 "
8.	Mica. " " < 0.01 "

As a torsion apparatus, a glass thread (length 30 c.m.) was used. At its lower end it carried a plane mirror, and above it was fastened in an iron clamp in the interior of the arrangement of Fig. 4 in the neck of the globe. In order to fasten the torsion thread *without cement*, its ends were secured between two pieces of ignited asbestos cardboard and fastened above by means of the clamp, and below by a platinum ring to the mirror support.

The mirror was set in a thin aluminium setting, blackened with platinum chloride, and was platinised by deposition at the cathode, as even a covered silver mirror soon becomes destroyed by mercury fumes. Wellmann-Martin's method of illuminating the scale has proved most useful in overcoming the feeble reflection of such a mirror and the effects of the interposition of the arched wall of the glass globe.

For the determination of the direction force from observations of the oscillations, the torsion thread was removed from the globe, the vane apparatus taken away, and the thread loaded with a copper-wire 4 c.m. long and having a mass of 0.314 gm.

The observations were made with three different torsion threads, whose direction forces were so chosen that if the scale distance were 1200 divisions the blank vanes gave a double deflection of 40 to 90 divisions. The three kinds of vane apparatus were found to have oscillation periods of fifteen, thirty-five, thirteen seconds respectively.

A Kahlbaum's pump was used to exhaust the globe. The measurements with a McLeod and Kahlbaum's manometer gave as result that a partial atmospheric pressure of 0.0001 m.m. (scarcely a fifteenth of mercury vapour pressure at the temperature of the room) could easily be obtained.

To obtain a still higher degree of exhaustion, the following method was employed:—Some mercury, *Q*, was poured into the globe *B*, the pump was started, and the mercury was warmed about 5° C. above the temperature of the room by means of a water-bath, *K*, placed under *B*; the mercury distils into the pump, which works continuously and draws with it the air in the globe *B*. If, by raising the mercury in the barometer tube, *V*, the globe is shut off from the pump and the dry vessel, *F*, only mercury vapour remains behind in the globe. By the usual method of cooling with ice and salt in *K*₁ and *K*₂ the tension of the mercury vapour can be made very small.

The quantity of energy of radiation incident on the vane was measured by a calorimeter. The lamp with the mirror apparatus (Fig. 1) was drawn so far back on the sliding base that the vane apparatus could be replaced by a diaphragm, *D* (Fig. 6 or Fig. 7), which was exactly the same size as each vane (*d* = 5 m.m.); all rays which passed through the diaphragm *D* were absorbed by a calorimeter. In these measurements, a glass disc, *G*, compensated for the reflection from the glass wall of the globe; it was interposed between the diaphragm and the calorimeter in order to stop the radiation of heat from the diaphragm.

The first calorimeter (Fig. 6) consisted of a copper block, *C*; the vertical hollow of this is filled with mercury, and in it is placed the bulb of a small thermometer, *T*, graduated in 1/10° C.; the absorbing surface was blackened. The total water equivalent of the calorimeter was 3.13 grms. (the specific heat of copper taken as 0.093).

The second calorimeter (Fig. 7) was a copper cylinder of similar construction with a water equivalent of 3.61 grms.; its absorbing surface was gilded and then platinised; it was placed in a brass vessel in a water-bath of about 1 litre capacity, which was provided with a stirrer, *R*.

In order to cool the calorimeter below the temperature of the water-bath before beginning the experiment, a few drops of ethyl ether were poured by means of the glass tube, *A*, into the conical opening of the calorimeter, and a strong current of air drawn through the brass vessel by means of indiarubber bellows, *B*.

The measurements gave as a result that the quantity of energy of radiation incident on the diaphragm (*d* = 5 m.m.) amounts to 1.2 to 1.8 gm.-cals. per minute, *i.e.*, that this intensity amounts to from twice to three times the total radiation of the sun on the earth's surface.

A Ritchie's photometer serves to measure the reflection of the metal leaf employed (Fig. 8). The light of two small incandescent lamps, *L*₁ and *L*₂, passed through the diaphragms, *D*₁ and *D*₂ (diameter 3 m.m.), and fell on a little prism of chalk, *K*, whose edges are observed through a magnifying glass, *B*. The lamp *L*₁ was adjusted till the brightness of the two lamps appeared equal; then *L*₂ was turned through an angle of about 130° towards *L*₂, the diaphragm *D*₂ was closed from without by the metal leaf under examination, and again *L*₁ adjusted to *L*₂, where its brightness equalled that of *L*₂. For the angle of incidence of 25°, the reflecting power, *Q*, of the metal leaf is given by—

$$Q = (KL : KL_1)^2.$$

(To be continued).

ON THE RELATION OF THE VISCOSITY OF MIXTURES OF SOLUTIONS OF CERTAIN SALTS TO THEIR STATE OF IONISATION.*

By JAMES BARNES, B.A., Dalhousie College, Halifax, N.S.

(Concluded from p. 31).

Mixtures of Solutions.

As there is no change of volume on mixing the constituent solutions of the above electrolytes of the concentrations given below (see *Trans. N.S. Inst. Sci.*, 1895-96, ix., 125; also 1897-98, ix., 297, and 310), and as the solutions mixed were of equal volume and also equimolecular, the expression (2) for the value of a property in the case of a mixture of two electrolytes with a common ion, reduces to:—

$$P = P_w + \frac{n}{2} [k_1(1 - a_1) + l_1a_1 + k_2(1 - a_2) + l_2a_2] \quad \dots (3).$$

where *n* is the concentration of the solutions, and the *k*'s and *l*'s have the values obtained above for simple solutions

* Transactions of the Nova Scotian Institute of Science, x., p. 113.

of the respective electrolytes. For the application of this equation to the calculation of the viscosity of a mixture, all the quantities required are known except the α 's, the ionisation coefficients in the mixture.

Determination of Ionisation Coefficients in the Mixture.

The method proposed by Professor MacGregor (*Trans. N.S. Inst. Sci.*, 1895-96, ix., 101; also 1898-99, x., 68) for finding the ionisation coefficients in a mixture of two electrolytes having an ion in common, is by solving graphically the following equations:—

$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2} \dots \dots \dots (4),$$

$$N_1 V_1 + N_2 V_2 = 1 \dots \dots \dots (5),$$

$$\frac{\alpha_1}{V_1} = \int_1(V_1) \dots \dots \dots (6),$$

$$\frac{\alpha_2}{V_2} = \int_2(V_2) \dots \dots \dots (7),$$

where the electrolytes are denoted by 1 and 2, the concentrations (in grm.-equivalents per litre) of the mixture with respect to them by N_1 and N_2 respectively, their ionisation coefficients by α_1 and α_2 , and their regional dilutions (in litres per grm.-equivalent) by V_1 and V_2 , the regional dilutions being the dilutions of the electrolytes in the regions which they are supposed to occupy in the mixture, or the dilutions of the constituent isohydric solutions.

His graphical mode of solving these equations involves the drawing of dilution-ionic-concentration curves, which, as they have great curvature for moderately dilute solutions, cannot be drawn with great accuracy unless a large number of observations of the conductivity are available. As mentioned above, extensive series of observations of the conductivity in the case of the salts under consideration were available; but they were all made at 18° C., and required therefore to be reduced to 25° C. before they could be used. In order to reduce this labour as much as possible I devised another mode of solution which requires only a comparatively small number of observations. It is based on the fact that the specific-conductivity-concentration curve of an electrolyte exhibits only slight curvature, and can therefore be drawn with fair accuracy from a small number of observations.

The above equations may be expressed in terms of specific conductivity and concentration as follows:—Since

$$\frac{\alpha_1}{V_1} = \frac{\mu_1}{V_1 \mu_{\infty 1}} = \frac{k_1}{\mu_{\infty 1}} \dots \dots \dots (8),$$

and—

$$\frac{\alpha_2}{V_2} = \frac{k_2}{\mu_{\infty 2}} \dots \dots \dots (9),$$

where k_1 and k_2 are the specific conductivities of the electrolytes in the regions which they respectively occupy in the mixture, and the μ_{∞} 's the specific molecular conductivities at infinite dilution for each electrolyte, equation (4) becomes:—

$$\frac{k_1}{\mu_{\infty 1}} = \frac{k_2}{\mu_{\infty 2}} \text{ or } k_1 = \frac{\mu_{\infty 1}}{\mu_{\infty 2}} k_2 \dots \dots (10).$$

From equation (5) we obtain:—

$$\frac{N_1}{C_1} + \frac{N_2}{C_2} = 1 \dots \dots \dots (11),$$

where C_1 and C_2 are the regional concentrations. Equations (6) and (7) are based on the fact that at a definite temperature the conductivity is a function of the concentration alone. They therefore take the following forms:—

$$k_1 = f_1(C_1) \dots \dots \dots (12),$$

and—

$$k_2 = f_2(C_2) \dots \dots \dots (13).$$

There are thus four equations (10—13) for the determination of the four unknown quantities:— k_1 , k_2 , C_1 , and C_2 .

These equations can be solved graphically. Equation (12) is employed by drawing a curve having as abscissae the values of the specific conductivities and corresponding values of the concentrations as ordinates. Before equation (13) is used the values of the conductivities are multiplied by the constant $\frac{\mu_{\infty 1}}{\mu_{\infty 2}}$. Then these new values are plotted

against the corresponding concentrations, on the same co-ordinate paper, to the same scale as employed for equation (12). From these two curves one finds by inspection two points, one on each curve, having a common abscissa, according to equation (10), and ordinates (C_1 and C_2) such that by substituting their values in equation (11) it will be satisfied. These points can be found after two or three trials. Thus one has determined k_1 , C_1 , and C_2 ; k_2 being found by multiplying k_1 by the constant $\frac{\mu_{\infty 1}}{\mu_{\infty 2}}$. The α 's are now obtained from equations (8) and (9); for the reciprocals of the C 's give the V 's.

Results of the Calculations on Mixtures.

The following Table VI. contains the requisite data for the calculation, by formula (3), of the viscosity of mixtures of solutions of the salts under consideration; and it shows the agreement of the values thus calculated with the observed values. The ionisation coefficients of the salts in the mixture are determined as above, and the concentrations are expressed as in the former tables.

TABLE VI.—Viscosity at 25° (Kanitz).

Concentration constituent solutions.		Ionisation coefficients in mixture.		Observed values.	Calculated values.	Difference.
KCl.	NaCl.	KCl.	NaCl.			
1.0	1.0	0.745	0.667	1.0390	1.0419	+0.0029
0.5	0.5	0.775	0.728	1.0180	1.0173	—0.0007
0.25	0.25	0.807	0.783	1.0070	1.0069	—0.0001
KCl.	$\frac{1}{2}$ BaCl ₂ .	KCl.	$\frac{1}{2}$ BaCl ₂ .			
1.0	1.0	0.756	0.552	1.0429	1.0533	+0.0104
0.5	0.5	0.779	0.613	1.0159	1.0220	+0.0061
0.25	0.25	0.811	0.675	1.0049	1.0082	+0.0033
$\frac{1}{2}$ K ₂ SO ₄ .	$\frac{1}{2}$ Na ₂ SO ₄ .	$\frac{1}{2}$ K ₂ SO ₄ .	$\frac{1}{2}$ Na ₂ SO ₄ .			
1.0	1.0	0.535	0.434	1.1660	1.1670	+0.0010
0.5	0.5	0.597	0.517	1.0773	1.0768	—0.0005
0.25	0.25	0.641	0.604	1.0334	1.0354	+0.0020
$\frac{1}{2}$ K ₂ SO ₄ .	$\frac{1}{2}$ CuSO ₄ .	$\frac{1}{2}$ K ₂ SO ₄ .	$\frac{1}{2}$ CuSO ₄ .			
1.0	1.0	0.559	0.152	1.2240	1.2423	+0.0183
0.5	0.5	0.612	0.210	1.1060	1.1107	+0.0047
0.25	0.25	0.668	0.256	1.0485	1.0510	+0.0025

Kanitz regards his observed values as affected by a possible error of ± 3 in the third decimal place. Considering the many calculations necessary to obtain the calculated values—first, in finding the specific molecular conductivity at infinite dilution for 25° C., and also ionisation coefficients at 25° from the data at 18°, and then in the determination of the ionisation coefficients of the salts in the mixture by the graphical method—the agreement between the observed and the calculated values (calculated, it should be noted, with the ionisation constants obtained for the simple solutions), is very satisfactory, especially in the case of solutions of potassium chloride and sodium chloride, and solutions of potassium sulphate and sodium sulphate, where the differences are all within the limit of experimental error. In the case of the stronger solutions of potassium chloride and barium chloride, and of potassium sulphate and copper sulphate, the differences are not within the limit of error; but a close agreement, as was pointed out in the beginning, could not be expected. It will be noticed, however, that the differences in these cases diminish and approach the experimental error as concentration diminishes. Observations on the viscosity of weaker solutions of these salts were not available.

From these results, therefore, it may be concluded, that

the viscosity of mixtures of dilute solutions of the salts under consideration can be predicted, by the aid of a dissociation theory, within the limit of experimental error, from data as to the viscosity and conductivity of the constituent solutions only.

ON PYRITE AND MARCASITE.*

By H. N. STOKES.

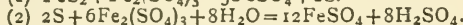
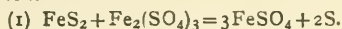
(Continued from p. 34).

II. BEHAVIOUR OF PYRITE AND MARCASITE TOWARD FERRIC SOLUTIONS (continued).

Ferric Sulphate Oxidation Method.

OWING to the tediousness of the gravimetric methods and of the SO_4 determination in the presence of iron, I have adopted a much more expeditious indirect method, which involves the use of ferric ammonium alum and titration with potassium permanganate.

Principle of the Method.—The oxidation of FeS_2 by $\text{Fe}_2(\text{SO}_4)_3$ may be regarded as taking place by two independent reactions:—



If the reaction be carried out in the presence of an excess of FeS_2 to complete reduction of the ferric salt, it is easily seen that equation (1) holds even if the theory of Brown be true, that the iron in pyrite is partly ferric, for in this case the ferric salt formed will in turn be reduced by the excess of pyrite. Upon the extent to which the second reaction takes place, as compared with the first, depends the percentage of sulphur oxidised in that portion of the mineral which is decomposed.

If a ferric solution containing a known amount of iron be boiled with an indefinite excess of FeS_2 under appropriate precautions, and if the increment of iron in the solution be then determined, as well as the ferrous salt formed, this increment gives the amount of sulphide decomposed: three times this increment gives the quantity of ferrous salt formed in equation (1); while any excess of ferrous salt is that formed by oxidising sulphur to sulphuric acid as in equation (2). From these data the percentage of sulphur oxidised may be computed.

Deduction of an Expression for Oxidised Sulphur.

It is unnecessary to know the absolute quantities of iron and sulphur involved in these reactions, or the strength of the permanganate solution. It suffices, in deducing an expression for the oxidised sulphur, to employ symbols expressing the permanganate equivalent of the iron, and the symbols used represent simply the volumes of permanganate consumed by a given volume of the solution.

For a given volume let—

a = iron in the original solution,

b = resulting ferrous iron,

c = resulting total iron.

Then—

$c - a$ = increment of iron resulting from decomposition of FeS_2 ,

and—

$2\left(\frac{31.83}{55.60}\right)(c - a)$ = total sulphur in decomposed sulphide (A).

Also,—

$3(c - a)$ = ferrous iron produced according to equation (1).

and—

$b - 3(c - a)$ = ferrous iron produced by oxidation of sulphur.

According to equation (2), 1 atom of sulphur requires

for oxidation 6 atoms of ferric iron, producing 6 atoms of ferrous iron; hence,—

$$\frac{x}{6} \cdot \frac{31.83}{55.60}(b - 3(c - a)) = \text{sulphur oxidised} \quad (B).$$

Calling the percentage of sulphur oxidised p , we obtain from (A) and (B)—

$$p = \frac{\frac{100}{6} \cdot \frac{31.83}{55.60}(b - 3(c - a))}{2\left(\frac{31.83}{55.60}\right)(c - a)} = \frac{8.333b}{c - a} - 25.$$

It thus appears that three titrations suffice to determine the percentage of sulphur oxidised, and that neither the amount of FeS_2 , the volume of the ferric solution used, nor the absolute titre of the latter or of the permanganate need be known. As, however, the proportion of sulphur oxidised varies with the strength of the ferric solution, the extent of reduction, and the temperature, it is necessary, in order to obtain comparable results, to use a solution of standard composition and a standard temperature, and to continue the action to complete reduction.

Standard Solution and Temperature.

The standard solution contains 1 grm. ferric iron per litre, and is prepared by dissolving in water 8.61 grms. clear crystals of pure ferric ammonium alum, adding 16 c.m.³ 25 per cent sulphuric acid, and diluting to 1 litre. One hundred c.m.³ of this solution must show a decided change of colour with one drop of the permanganate solution, containing about 1.5 grms. per litre, and must be free from nitrate. The sulphuric acid is added to prevent precipitation of basic salt. The experiment is conducted at the boiling temperature. The strength of the ferric solution may vary 1 per cent without appreciable influence, and at least 99.5 per cent must be reduced.

Oxidation Coefficient.

The percentage of sulphur oxidised under these conditions, and with the precautions explained in detail below, may be called briefly the *oxidation coefficient* of the pyrite or marcasite. The oxidation coefficient of pyrite varies between 60 and 61, and that of marcasite between 16.5 and 18. The oxidation coefficients of mixtures of the two indicate the relative amount of each present, by reference to an empirical curve obtained with artificial mixtures of known composition. A theoretical deduction of the relative proportions from the oxidation coefficient is impossible in the absence of the necessary physical data.

Theory of the Reaction.

The mass law states that the active mass of a solid phase is constant; hence, the final composition of the resulting solution must be the same, irrespective of the relative amount of reagent and sulphide used, provided only that the latter, the solid phase, be always in excess. With more, or more finely powdered, material*—that is, with a relatively greater exposure of surface, equilibrium is sooner reached, but the composition of the resulting solution, and therefore the percentage of sulphur oxidised, is the same. It is unnecessary either to weigh the material or to measure the liquid accurately, but in order to make unavoidable experimental errors as nearly as possible constant, it is desirable always to employ approximately equal quantities, and to boil for nearly equal times.

Influence of Concentration.

Since the equation expressing the oxidation of the sulphur is of a higher order than that denoting the oxida-

* Ostwald (*Zeit. Physik. Chemie*, 1900, vol. xxiv., p. 495) has shown for certain cases that an extremely finely powdered substance is more soluble than the same in coarser particles, and that the composition of the resulting solution is therefore subject to slight variations. Such effects were looked for in the present instance by using coarse and very fine material obtained by sedimentation, but if they exist they are smaller than the errors of the method.

* From the *Bulletin of the U.S. Geological Survey*, No. 186.

tion of the iron, it follows that the rate of oxidation of the sulphur must fall off more rapidly than that of the iron, with decreasing concentration of the ferric salt; hence, the value of p must constantly decrease as reduction proceeds, and comparable results can be obtained only by carrying the reduction to completion. This is shown in the following cases, where the experiment was stopped after partial reduction:—

Results of Experiments showing Constantly Decreasing Value of p as Reduction Proceeds.

Pyrite.		Marcasite.	
Fe reduced.	p .	Fe reduced.	p .
Per cent.	Per cent.	Per cent.	Per cent.
67.8	71.4	69.2	23.3
88.7	65.2	78.5	22.5
90.5	64.9	100.0	16.2
95.2	63.2		
99.5	61.5		
100.0	60.4		

Influence of Temperature.

The influence of temperature on p is shown by the following experiments at 20° and at boiling temperature, the reduction being complete in each case:—

Results of Experiments showing Influence of Temperature on p .

	Temperature.	p .
Pyrite	20°	80.8 per cent
	100°	60.4 "
Marcasite	20°	30.6 "
	100°	17.4 "

From the variation in the relative oxidation of the sulphur with concentration and temperature, it appears certain that no single equation expresses the oxidation of pyrite and marcasite by ferric salts to ferrous sulphate, sulphur, and sulphuric acid, but that it is the result of two, or possibly three, independent reactions of different orders, which produce results varying according to circumstances. It is therefore extremely probable that other oxidising agents, as atmospheric or dissolved oxygen, behave in a similar manner. The oxidation with separation of free sulphur presents no difficulties; as is well known, finely powdered pyrite and marcasite on exposure to the air for a short time give free sulphur, which can be detected by extraction with ether, and the formation of sulphur dioxide has been noted by various observers; finely divided moist marcasite evolves it strongly when heated on the water-bath. The difficulty is rather to account for the complete oxidation of the sulphur usually occurring in nature. Whether with stronger solutions and continued re-oxidation by air, or the presence of retarding agents, 100 per cent can be reached can not be stated at present, and experiments bearing on this point are desirable.

Reasons for the Different Behaviour of Pyrite and Marcasite.

The different proportion of sulphur oxidised under identical conditions in the two cases is doubtless due to the different solubilities of pyrite and marcasite, or at least the different rates at which they are attacked. That the sulphur is not completely oxidised is due to its smaller oxidation rate under the given conditions. The iron is attacked so fast that the oxidation of the sulphur falls behind, and a portion is liberated as free sulphur, which, as my experiments show, is scarcely oxidised by the boiling ferric solution when collected to aggregates of sensible size. This phenomenon is a familiar one when precipitated sulphides are treated with nitric acid; a portion of the sulphur is oxidised, and the remainder is liberated. When a ferric salt is reduced by hydrogen sulphide the sulphur of the latter is partly liberated, but a very con-

siderable part is oxidised to sulphuric acid.* Whatever retards the solution of the sulphide without affecting the concentration of the oxidiser gives more time for the complete oxidation of the sulphur. This may be brought about by certain salts in solution or by a difference of physical structure in the crystals. Pyrite dissolves more slowly than marcasite, hence its sulphur is more completely oxidised. Under conditions where the solution is very slow, it may perhaps approximate completeness in both cases, a subject well worthy of investigation from its bearing on the oxidation of pyrites in nature.

Further Applications of the Method.

In general, when a mineral is composed of two or more elements, each capable of oxidation, but at different rates, there will be certain conditions under which one will be oxidised to a greater extent than the other, and the amount of this difference may often be determined by analysis of the solution. If the compound is dimorphous, one form will be more soluble than the other, and this will show a greater difference in the degree of oxidation of the two constituents than the less soluble form. The above method therefore makes it possible to distinguish not only between dimorphous sulphides but other dimorphous compounds, such as arsenides, and to determine their relative amounts in mixtures. It should also be possible to determine whether certain complex minerals are mixtures of two distinct kinds of molecules, or whether all the components are combined in one molecule. FeAsS, for example, should show a behaviour different from that of a mixture FeS₂ and FeAs₂ in equimolecular proportions. When the metal is more slowly oxidised than the non-metallic constituent a separation of a portion of the former may be expected. Gold sulphide, for example, might give sulphuric acid and free gold. As pointed out below, it is possible to ascertain in certain cases the form of combination of constituents which exist only as impurities; in a 3 per cent cupriferous pyrite, chalcopyrite can be distinguished from chalcocite and bornite, a determination which could not be made by analysis.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1901.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 1st to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

* "Gmelin's *Kraut*," vol. i., Part 2, p. 219. I have found that when a 1 per cent boiling solution of ferric chloride is reduced by hydrogen sulphide very nearly one-third of the reduction is effected by the sulphur.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us during the month, all were found to be clear, bright, and well filtered.

For the third time only during this year we have to record an excess of rain. The rainfall measured at Oxford during December was 3.29 inches, the average is 2.16 inches; this gives an excess of 1.13 inches, and reduces the previous deficit to 3.13 inches, or 12.3 per cent for the whole year, on the thirty-five years' average, as will be seen by Table A.

Our bacteriological examinations of 494 samples have given the results recorded in the following table; we have also examined 37 other samples, from special stand-pipes, wells, &c., making a total of 531 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	387
New River, filtered (mean of 120 samples) ..	18
Thames, unfiltered (mean of 24 samples) ..	4065
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 270 samples) ..	31
Ditto ditto highest	324
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	446
River Lea, from the East London Company's clear-water wells (mean of 32 samples) ..	14

Of the 422 samples of the impounded and filtered water supplied to London and examined bacteriologically during

TABLE A.—Rainfall in Inches at Oxford, Month by Month, during the Year 1901.

	Actual fall. Inches.	Mean of 35 years. Inches.	Difference from the mean.	
			Inch.	Inch.
January ..	1.04	2.08	-1.04	—
February ..	1.31	1.80	-0.49	—
March ..	1.44	1.47	-0.03	—
April ..	1.96	1.61	—	+0.35
May ..	1.24	1.75	-0.51	—
June ..	1.52	2.10	-0.58	—
July ..	4.66	2.49	—	+2.17
August ..	2.12	2.38	-0.26	—
September ..	1.86	2.39	-0.53	—
October ..	1.18	2.76	-1.58	—
November ..	0.54	2.30	-1.76	—
December ..	3.29	2.16	—	+1.13
	22.16	25.29	-6.78	+3.65

TABLE B.—Table showing Average Monthly Bacterial Variations during the Year 1901.

Month.	Thames, unfiltered.	Thames- derived Companies, filtered.	New River, unfiltered.	New River, filtered.	River Lea, unfiltered.	River Lea (East London), filtered.
January ..	4069	49	671	28	450	16
February ..	5310	26	800	5	172	18
March ..	2303	27	593	10	315	43
April ..	2076	15	176	6	177	15
May ..	852	9	106	6	209	13
June ..	1371	26	204	8	488	56
	2663	25	425	10	302	27
						Mean of 1st 6 months.
July ..	5560	35	383	13	837	40
August ..	1646	22	284	13	223	16
September ..	873	19	215	7	266	17
October ..	865	13	173	4	155	12
November ..	1909	25	280	10	202	13
December ..	4065	31	387	18	446	14
	2486	24	287	10	355	18
						Mean of 2nd 6 months.
	2575	24	356	10	328	22
						Mean of 12 months.

TABLE C.—Average Number of Microbes in the Filtered London Waters for the Past Five Years.

	Thames-derived Companies.	New River.	River Lea.
1897 ..	46	32	62
1898 ..	34	30	25
1899 ..	27	15	20
1900 ..	21	9	10
1901 ..	24	10	22

TABLE D.—1901.—Averages of the Supplies derived from the River Thames.

	Common salt per gallon.	Nitric acid per gallon.	Hardness, Degrees.	Oxygen required per gallon.	Organic carbon per gallon.	Organic carbon per gallon.	Colour. Brown : Blue.
	Means.	Means.	Means.	Means.	Means.	Maxima.	Means.
January ..	2.194	1.047	16.12	0.058	0.161	0.253	21.7 : 20
February ..	2.189	1.101	16.46	0.053	0.148	0.185	17.4 : 20
March ..	2.227	1.035	15.64	0.056	0.172	0.237	18.5 : 20
April ..	2.193	0.796	15.20	0.068	0.177	0.234	19.4 : 20
May ..	2.109	0.776	14.68	0.042	0.106	0.139	11.6 : 20
June ..	2.112	0.711	14.12	0.040	0.090	0.137	10.1 : 20
July ..	2.160	0.717	13.28	0.039	0.075	0.100	9.5 : 20
August ..	2.047	0.634	12.85	0.040	0.076	0.090	9.6 : 20
September ..	2.243	0.639	12.75	0.035	0.080	0.094	7.2 : 20
October ..	2.335	0.631	13.83	0.036	0.088	0.103	6.7 : 20
November ..	2.406	0.940	15.19	0.035	0.094	0.115	8.8 : 20
December ..	2.506	0.991	15.43	0.043	0.104	0.152	13.4 : 20

the past month, 21 samples, or 4.9 per cent, were sterile. Eleven samples contained more than 150 microbes, while twenty-seven samples, or 6.3 per cent, contained over 100 microbes per c.c. The mean number of microbes in the twenty-seven excess samples was 185, against a corresponding mean of 154 in fourteen excess samples during November.

During the past year we have examined 6893 samples of London waters bacteriologically, as compared with 6731, 4792, and 3500 respectively in the three previous years. We have also made 2522 chemical analyses of London waters throughout this period, making a total of 9415 samples examined during the year.

The results of the filtration of the London waters are given in Tables B, C, and D.

Table B shows that during the first six months the Thames-derived Companies' clear-water wells contained on the average 25 bacteria per c.c., while the New River and River Lea supplies contained respectively 10 and 27. During the second six months, the number of bacteria in the waters from the three sources were respectively 24, 10, and 18.

An examination of the accompanying tables of the average composition, chemical and bacteriological, of the London water supply, proves that the quality on the whole was excellent, and that the high standard of previous years was well maintained during 1901. The care and attention which has been given to the general character of the supply is seen from the large number of samples—nearly 10,000—examined during the year.

It is remarkable that the rainfall in the Thames Valley was 12.3 per cent below the thirty-five years' average, a deficit substantially the same as that which occurred in the year 1900. We have had now seven yearly periods in which a deficiency of rain has occurred in the Thames Valley, as measured at Oxford, the aggregate deficit amounting to no less than 25.31 inches. Under these exceptional circumstances it is worthy of remark that London has suffered no restriction in the matter of supply, although many towns in the country have experienced considerable inconvenience from having to curtail their consumption of water.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

THE CONSTITUTION OF TOURMALINE.*

By F. W. CLARKE.

(Concluded from p. 32).

IN these cases the low boric acid of the analyses and the uncertainties as to the significance of the water determinations account for the chief variations between observation and theory. There is another complication also, due to the fact that alternative expressions are possible between which it is very difficult to decide. In the tourmaline from Haddam Neck, Connecticut, analysed by Penfield and Foote, a somewhat different commingling of molecules seems to be necessary, partly on account of the higher proportion of lime in the mineral and partly on account of the fluorine. This tourmaline also admits of various alternatives in formulation, but it agrees well with the molecular mixture—

3. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Ca.Fe}_4\text{H}_4$,
10. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3(\text{AlOH}).\text{Al}_2\text{Li}_2\text{H}_4$,
1. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{Ca.A}_3\text{NaH}_2$,
6. $\text{Al}_5(\text{SiO}_4)_6(\text{BO}_2)_2.\text{BO}_3\text{NaH.A}_3\text{NaH}_2$;

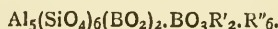
in which Ca is equivalent to a replacement of NaH. This mixture, with the group AlOH proportional to

fluorine, gives a good comparison between analysis and theory, thus—

	Found.	Reduced.	Calculated.
SiO_2	36.96	36.75	36.86
B_2O_3	11.00	10.94	10.74
TiO_2	0.03		
Al_2O_3	39.56	39.35	39.44
FeO	2.14	4.35	4.43
MnO	2.00		
MgO	0.15		
CaO	1.28	1.27	1.15
Na_2O	2.10	2.09	2.07
Li_2O	1.64	1.63	1.54
H_2O	3.10	3.62	3.77
F	1.13		
	101.09	100.00	100.00

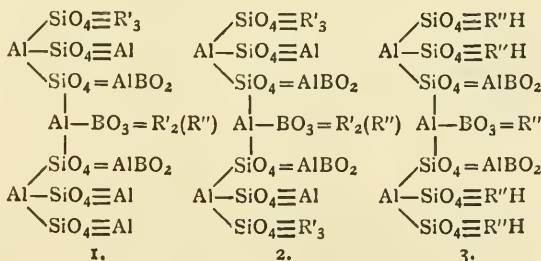
The theoretical amount of fluorine needed to replace hydroxyl in the assumed group, AlOH , is 0.97 per cent. Altogether, the comparison is fairly satisfactory.

One analysis by Riggs, that of the magnesite tourmaline from Hamburg, New Jersey, I have omitted from my discussion. In that tourmaline there are variations which I cannot readily account for, unless by assuming the presence in it of a molecule—



Such a molecule, written structurally, exhibits affinities to garnet rather than to the micas; and I prefer to await further evidence before committing myself to any definite formulation in this instance. As for the analyses published by Jannasch and Kalb, they fit in well with those of Riggs, and are amenable to the same treatment.

At first glance, some of the formulæ which I have proposed may seem to be complex; but they are all of the same type, and can be reduced to a few general expressions, as follows:—



These formulæ cover all of the established variations in the composition of tourmaline; they render the various replacements or isomorphous admixtures intelligible, and they indicate the directions into which the species commonly alters. There is one objection to them, namely, that one of the end-products contains no alkali metal, and no alkali-free tourmaline is known. The same objection applies to the Penfield-Foote formula, as will be seen by anyone who attempts to apply it in the discussion of the iron tourmalines. Under either system of formulation the existence in tourmaline of alkali-free salts must be assumed.

One further possible advantage in the proposed formulæ remains to be pointed out. All of the chemists who of late years have discussed the composition of tourmaline agree in adopting the ratio between silicon and boron of 2:1, or $4\text{SiO}_2:\text{B}_2\text{O}_3$. And yet many of the analyses vary from this ratio to an extent which may not be due to experimental errors. For example, from among Riggs's analyses the following cases show large variations, the boron being too low. I give the silica and boric oxide as determined, the boric oxide as calculated from the silica by the accepted ratio, and the amount of variation between the two.

	SiO ₂	B ₂ O ₃ found.	B ₂ O ₃ calculated.	Difference.
Rumford, red ..	38.07	9.99	11.10	-1.11
Paris, black ..	35.03	9.02	10.22	-1.20
Monroe, brown ..	36.41	9.65	10.62	-0.97
Brazil, green ..	36.91	9.87	10.76	-0.89
Auburn, colourless	38.14	10.25	11.12	-0.87

In the analyses by Jannasch and Kalb the following examples are very striking:—

	SiO ₂	B ₂ O ₃ found.	B ₂ O ₃ calculated.	Difference.
Snarun	35.64	9.93	10.40	-1.47
Mursinka	34.88	8.94	10.17	-1.23
Buckworth	35.50	8.34	10.35	-2.01
Brazil	37.05	9.09	10.81	-1.72

It would hardly be wise to dismiss these variations as due to errors, especially when the summation of the analyses is good and the analysts are known to be trustworthy. Such errors on the part of either Jannasch or Riggs would be almost incredible, and I am therefore inclined to believe that the analyses are good, and that we should seek a cause for the variations. In my scheme of formulation the bi-valent group of atoms =Al—BO₂ occurs. Replace this in part by the similar groups =Al—OH and =Al—F, and the variations are accounted for. This supposition satisfies the analyses completely, and covers the ground. It is in accord with all the evidence, even though its validity may not be definitely proved. By its application to the discussion of the analyses, the divergences between the calculated composition and the composition as found can be notably diminished.

But although the formulæ which I have adopted serve to express the composition of all tourmalines, they still leave room for alternatives. Penfield and Foote, as well as myself, assume that tourmaline is a mixed salt containing distinct boric and silicic radicles. Future investigation may prove that it is really derived from a complex boro-silicic acid, as yet unknown; and the same conception may be true of other species, such as axinite, datolite, danburite, cappelinite, &c. A series of boro-silicic acids is theoretically conceivable; and until this question has been considered, the constitution of all the minerals above mentioned must be regarded as unsettled.

EXPERIMENTS RELATIVE TO THE CONSTITUTION OF PECTOLITE, PYROPHYLLITE, CALAMINE, AND ANALCITE.*

By F. W. CLARKE and GEORGE STEIGER.

In a series of investigations by Clarke and Schneider, which were carried out in the laboratory of the United States Geological Survey between 1889 and 1892 (*Bull. U.S. Geol. Survey*, No. 78, p. 11; *Ibid.*, No. 90, p. 11; *Ibid.*, No. 113, p. 27), a number of reactions were examined which shed some light upon the constitution of several natural silicates. The work then begun was unfortunately interrupted for several years; but it is now resumed, with the hope that it may be pushed considerably further.

Two of the reactions studied by Clarke and Schneider were of peculiar interest. First, in the case of talc, it was found that one-fourth of the silica could be liberated by ignition; and that the fraction thus set free was measurable by solution in aqueous sodium carbonate. This reaction suggests that other acid metasilicates may behave in a similar way, and that we perhaps have a means of discrimination between such salts and other compounds which simulate them. In other words, an acid metasilicate may be experimentally distinguished from a pseudo-metasilicate by the way in which it splits up when

ignited. Evidence bearing upon this supposition will be found in the present paper.

The second of the reactions just referred to is that between di-ammonium chloride, at its temperature of dissociation, and various silicates (*Bull. U.S. Geol. Survey*, No. 113, p. 34). This involves, in part at least, the action of dry gaseous hydrochloric acid upon the compounds which are studied; and different minerals are very differently attacked. Some are almost completely decomposed, others are affected but slightly; and here again there seems to be a method of diagnosis which deserves further attention. Both reactions suggest the main purpose of the investigation; which is, the fractional analysis of silicates by means of various reagents, in order to gain evidence bearing upon their chemical structure. The evidence, at least is of value, whether the interpretation of it be right or wrong. Each fact helps to the ultimate solution of the central problem, the problem of constitution.

Pectolite.

The pectolite which was chosen for examination was the well-known radiated variety from Bergen Hill, New Jersey. The mineral was in long, white needles, and apparently quite pure; but the analysis shows that it contained some carbonate as an impurity. Enough of the material was ground up to furnish a uniform sample for the entire series of experiments, and the work properly began with a complete analysis. The results obtained are as follows:—

Analysis.

SiO ₂	53.34
Al ₂ O ₃	0.33
CaO	33.23
MnO	0.45
Na ₂ O	9.11
Total H ₂ O	2.97
CO ₂	0.67

100.10

Fractional Water.

At 105°	0.27
At 180°	0.16
At 300°	0.22
At redness	2.32

2.97

All of the water was given off at a barely visible red heat; and the figures show that practically all of it is constitutional, a fact which perhaps hardly needed re-verification. The analysis gives the accepted formula for pectolite, $\text{HNaCa}_2\text{Si}_3\text{O}_9$. Does this represent, as is commonly assumed, a true metasilicate? If it does, we should expect that ignition would split off silica proportional to the acid hydrogen, or one-sixth of the total amount. To answer this question several portions of the pectolite were sharply ignited, to complete dehydration, and then boiled each for fifteen minutes with a solution of sodium carbonate containing 250 grms. to the litre. In the extract so obtained the silica was determined; and three experiments gave the following percentages:—

8.06

8.67

8.42

Mean, 8.68

One-sixth of the total silica is 8.89 per cent; and the experiments, therefore, justify the original expectation. The belief that pectolite is a metasilicate is effectively confirmed.

Upon the unignited pectolite the sodium carbonate solution has a slow decomposing action, both silica and bases being withdrawn. In two experiments fifteen minutes of boiling extracted 2.07 and 2.55 per cent of silica, and by a treatment lasting four days 4.80 per cent

* *Bulletin of the United States Geological Survey*, No. 167.

was taken out. With water alone similar results were obtained; the action being so rapid, although relatively slight, that peñolite, moistened, gives an immediate and deep colouration with phenolphthalein. By boiling the powdered peñolite with distilled water alone 1.65 per cent of silica was brought into solution, and the ignited mineral, similarly treated for fifteen minutes, gave 1.78 per cent. The extraction in these cases is really an extraction of alkaline silicate, as the two following experiments prove. In A the unignited peñolite was boiled for fourteen hours with distilled water; and in B the mineral after ignition was subjected to like treatment for four hours. The dissolved matter in each case was determined, with the subjoined results:—

	A.	B.
SiO ₂	2.98	3.03
CaO	0.30	0.10
Na ₂ O	0.81	1.50
	4.09	4.63

In A, no simple ratio appears; but in B the extracted silicate approximates very nearly to the salt Na₂Si₂O₅. In each instance the ratios vary widely from those of the original mineral, showing that actual decomposition and not a solution of the peñolite as such has occurred.

In the experiments upon peñolite the heating with dry ammonium chloride was omitted, for the data are already given in the original paper by Schneider and Clarke. In their experiments the mineral was thrice heated with ten times its weight of the reagent to above 350°, and then leached out with water. In the solution 20.50 per cent of lime and 6.95 of soda were found, with part of the manganese; showing that a very considerable decomposition had taken place. Possibly, by repeated treatments with ammonium chloride a complete decomposition might be effected, but this question is one upon which it seemed unnecessary to spend further time.

(To be continued).

CORRESPONDENCE.

ON THE MUTUAL ACTION OF ALUMINA AND FERRIC OXIDE AT INCIPIENT WHITE HEAT.

To the Editor of the Chemical News.

SIR,—In reference to the article on the above subject (CHEMICAL NEWS, lxxiv., 305), and Mr. Riggs's letter on the combination of ferric oxide and zinc oxide (CHEMICAL NEWS, lxxv., 24), it may be of interest to state that apparently zinc oxide also combines with aluminium oxide when a mixture of the two oxides is exposed to a full red heat.

For instance, when the precipitate thrown down by ammonia and ammonium sulphide in a solution containing zinc and aluminium is ignited sharply in a muffle, and then treated repeatedly with boiling concentrated hydrochloric acid, the alumina left insoluble retains considerable amounts of zinc oxide.

Similarly, by firing a heated mixture of metallic aluminium and excess of zinc oxide by means of a piece of magnesium ribbon, a dark grey mass is produced which shows no sign of fusion. On extracting this with hydrochloric acid a residue containing variable proportions of both zinc oxide and aluminium oxide is left behind. The composition of one substance obtained in this way, which appeared to be homogeneous under the microscope, was 86.00 per cent Al₂O₃ and 14.05 per cent ZnO.

The preparation of an actual compound, however, free from any excess of alumina, presents some difficulty.—I am, &c.,

ARTHUR G. LEVY.

London, January 18, 1902.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—I have addressed the enclosed to the President of the Institute of Chemistry.—I am, &c.,

A. WYNTER BLYTH.

To the President of the Council of the Institute of Chemistry.

SIR,—I have been solicited by more than one Fellow of the Institute to support their candidature as members of the Council. Those who have done so are I doubt not well fitted to be elected, but though I have been in my time on the governing body of many societies this kind of canvassing is entirely new to me, and appears so objectionable and so much against the best interests of the Institute that I earnestly ask the Council to take some means of suppressing it.

If the system is allowed to continue the vacancies that occur from time to time will not be filled by the most eminent, but by the most energetic—by those individuals who take the trouble to personally solicit the votes of the Fellows. The effect of this will be that the Council will cease to be respected.—I am, your obedient servant,

A. WYNTER BLYTH.

Town Hall, Marylebone Lane, W.

January 14, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiii., No. 27, December 30, 1901.

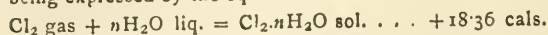
Critical Constants and Molecular Complexity of Higher Hydrocarbons.—Ph. A. Guye and Ed. Mallet.—The authors make a series of new measurements of critical constants of higher hydrocarbons, choosing in most cases bodies containing chemical groups, different from those previously examined by other experimenters, and amongst these compounds, in all possible cases, choosing those having a high critical temperature.

Extension of Kirchhoff's two Laws.—E. Carvallo.—The author's researches lead him to enunciate the two following laws:—(1). The total flow of current across any closed surface is zero. (2). The total electromotive force in a closed circuit is zero. The first of these laws can be found in Maxwell's formulæ, but it appears there to be the mathematical consequence of an hypothesis concerning the magnetic field produced by an open circuit and not as an experimental fact directly observed. The second law is apparently not included in Maxwell's formulæ. It is interesting to note that these two laws are merely extensions of Kirchhoff's two laws.

The Existence of Rays capable of being Reflected in Radiation Emitted by a Mixture of Chlorides of Radium and Barium.—Th. Tommasina.—Various observations led the author to believe that certain rays existed in the radiation emitted by certain radio-active bodies which were capable of reflection. By using a parabolic concave mirror of silvered copper the rays capable of reflection were separated from the others.

Heat of Formation of Chlorine Hydrate.—M. de Forcrand.—The author employs two methods for finding the heat of formation of chlorine hydrate. (1). A direct measurement of the quantity of heat produced when it is formed, and when it is decomposed; and (2) the calculation of this quantity by means of curves of dissociation. The number deduced from the curves was +18.16 cal.; direct measurement shows it to be +18.57 cal.; the

mean being +18.36 cals. This reaction is capable of being expressed by the equation—



The author hopes shortly to establish the exact composition of this hydrate.

NOTES AND QUERIES.

, Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Extracting Oil from Seeds.—A correspondent asks where he can obtain full particulars regarding the process of extracting oil from seeds by chemical means.

MEETINGS FOR THE WEEK.

- MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "The Purification and Sterilisation of Water," by Samuel Rideal D.Sc., F.I.C.
- TUESDAY, 28th.—Royal Institution, 3. "The Cell—its means of Offence and Defence—Immunity," by Allen Macfadyen, M.D., B.Sc.
- Society of Arts, 4.30. "To the Victoria Nyanza by the Uganda Railway," by Commander B. Whitehouse, R.N.
- WEDNESDAY, 29th.—Society of Arts, 8. "Technical Education as applied to Paper Making," by Clayton Beadle.
- THURSDAY, 30th.—Royal Institution, 3. "Recent Excavations at Delphi and in the Greek Islands," by A. S. Murray, LL.D., F.S.A.
- FRIDAY, 31st.—Royal Institution, 9. "The Ions of Electrolysis," by Prof. A. Crum Brown, D.Sc., F.R.S., &c.
- SATURDAY, Feb. 1st.—Royal Institution, 3. "Landmarks in the History of Opera" (with Musical Illustrations), by W. H. Hadow, M.A., Mus. Bac.

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THE CHEMICAL NEWS.

VOL. LXXXV., No. 2201.

BRONZING METHODS IN THE ALCHEMISTIC LEYDEN PAPYRI.

By ARTHUR JOHN HOPKINS.

THE importance to the history of Alchemy of the Papyri of Leyden V. and X., has been pointed out by M. Berthelot in his "Les Origines de l'Alchimie," and more recently in the "Collection des Anciens Alchimistes Grecs" (1888), in which he presents a translation of the recipes contained in the papyri, and in commenting on them shows their practical nature. In this oldest Alchemistic writing are such recipes for making alloys, and for cleaning the surfaces of the metals, as are used by metal-workers of the present day.

M. Berthelot is the first to show (a) that the "dream of alchemy" was, in the beginning, not a dream, but a very practical means of deceiving the people by substituting for true gold or silver, crude yellow or silver coloured paints, dyes, and varnishes; coloured alloys of probably recent discovery, and a copper-gold alloy from the surface of which the copper had been removed by "Royal Cement," leaving pure gold in relief; and (b) that the alchemists upon deceiving the people fell willing victims to their own deceptions by their ignorance of any individual properties and final tests for the metals, and by their claim of supernatural power in making the precious metals. "It is thus that the artisans, accustomed to make alloys simulating gold and silver, often with such perfection that they deceived themselves, ended by believing in the possibility of really making all sorts of metals by aid of certain combinations of alloys, and certain tricks, completed by the aid of supernatural powers, the sovereign masters of all transformations" ("Collection des Anciens Alchimistes Grecs," I., p. 73).

M. Berthelot is, however, unable to explain all the recipes. Some, which were apparently meant to be the frankest and most in detail, he marks as obscure. Some of course will always remain meaningless, as they are careless shop-recipes, often for secrecy intentionally obscured. But of those which are expressed in detail there still remain a few which seem capable of much meaning if we slightly extend the conception of the ancient worker in metal as presented to us by M. Berthelot. He has pointed out that the Egyptians conceived of silver and gold as a silvery or yellow metallic colour produced by certain synthetic processes. The object of this paper is to add to this conception by establishing the two following theses:—

- 1st. The Egyptian worker in metal was a bronzer.
- 2nd. Gold or silver was identified, not only by the colour of the metal, but also by the bronze which could be produced upon it.

The endeavour will be made to show by a detailed study of some of the hundred and one recipes of Papyrus X., together with one from Papyrus V., that these obscure recipes become more intelligible by looking on the Egyptian worker as a bronzer.

This proposition seems almost self-evident on reading the recipes with this changed conception as a guide. With the aid of the second proposition, some recipes become intelligible for the first time.

It is evident that the Egyptians having the bronzer's understanding of the metals would be more liable to self-deception, and this would tend further to explain their confidence in the possibility of transmutation.

As M. Berthelot has shown, the existence of "eleiron"

(native alloy of gold and silver), of asem (the artificial alloy of the same metals in varying proportions), of "asem" (falsitious, containing no gold or silver), as well as the absence of any exact tests for the metals, compelled the Egyptian artisan to hold the conception of the progressive relativity of the metals rather than the modern conception of strict individuality. Also the religious teaching of the transmigration of souls found additional expression in the transmutation of metals. What then did the Egyptian demand of his metals? Not that they should be modern gold and silver, for our definition of these metals was lacking. Asem, which was considered a metal and played so great a part in the transmutation theory, was sometimes like silver, sometimes like gold,* the property demanded of the metals being one of colour, or metallic sheen. The Egyptian longed for the golden sun-colour with which to adorn his temples, and the metallic colours were both brilliant and permanent. Brilliant colours, and, if possible, permanent colours, the child nations of the world have always delighted in. Gold, silver, purple, and (in Egypt) black are the delights of kings and peoples.

Before beginning the application of these theses to the recipes, it will be well to have a clear statement as to which bronzes are characteristic of silver and which of gold. Under treatment with sulphides in very dilute solution, silver takes a golden bronze, changing gradually to purple, then brown, but finally black. Quick bronzing generally produces an immediate black on silver, which is permanent ("oxidised silver"), and for this blackening of silver Egypt was noted. Pliny states ("Hist. Nat.," xxxiii., 46, Bohn translation):—"The people of Egypt stain their silver vessels that they may see represented in them their god Anubis, and it is the custom with them to paint, not to chase, their silver. This usage has now passed to our own triumphal statues even; and, a truly marvellous fact, the value of silver has been enhanced by deadening its brilliancy." Silver was identified both by its silvery colour and by its black bronze. The production of a black bronze was sufficient to establish the claim for an alloy that it was silver (or nearly silver), or even that it was standard silver ("Chemistry of Moses," 47; Berthelot, "Texte Grec," p. 309). Gold, on the other hand, besides its own colour sacred to the sun, was capable of taking bronzes of most brilliant shades—purple, violet, red, and iridescence.

In the following detailed study of the recipes of the Alchemistic Leyden Papyri from the standpoint outlined in the first portion of this paper, I have chosen the modern work of Arthur H. Hiorns ("Metal Colouring and Bronzing," Macmillan and Co., 1892), as authority for the conduct of different metals under processes as close as possible to those described in the alchemistic recipes. In following these recipes I am depending upon the accuracy of the French translation as presented by M. Berthelot in his brilliant work—the edition of the original Greek not being available. Had this translation been made with the conception of the processes of bronzing as a guide in the mind of the translator, it may be that some of the recipes which have been excluded from the following study could have been used to show still further evidence of the crude beginnings of the bronzer's art.

Papyrus V.—"Ἰωσις Χρυσῶν."

This is the only alchemistic recipe in Papyrus V. It is in two parts as follows:—

"Take some strong vinegar, thicken, take some —, 8 drachms of common salt, 2 drachms of alum shale, 4 drachms of litharge, rub with the vinegar for three days, separate by decantation, and use. Then add to the vinegar 1 drachm copperas, one-half obole of —,

* Of the twenty-four recipes in Papyrus X. for the preparation of "asem," nineteen would produce a white alloy, two a reddish-yellow alloy, while three are doubtful.

three oboles of calcite, one and one-half oboles of sory, a silique of common salt, two siliques of salt of Cappadocia. Make a layer with two quarters (of an obole?). Make it undergo the action of fire . . . until the layer breaks, immediately take the pieces, and regard them as refined gold."

"Having taken four leaves of gold, make foil of them, heat it, and immerse it in copperas rubbed with water, and with other dry copperas, cast (a portion) . . . with the dry material, another with the mixed material, discard the dross, and throw into —."

The second portion is incomplete. Of the first part, M. Berthelot states that it is cited in Papyrus X., Rx. 15, and that this establishes the connection between the two papyri. As a comparison of these two recipes is necessary, the first important recipe of Papyrus X. is given here:—

Rx. 15.—Colouring Gold.

"To colour gold to make it good for use. Misy and salt and vinegar left from the purification of gold. Mix all, and put into the vase (which contains) the gold described in the preceding preparation. Let it remain some time, and having removed (the gold) from the vase, heat it over charcoal; then put it again into the vase which contains the above-mentioned preparation; do this many times until it becomes good for use."

The title of the recipe in Papyrus V. is given in the original Greek, as there is doubt of its true meaning. M. Berthelot ("Collection des Anciens Alchimistes Grecs," I., p. 13, Note 5) has given four possible meanings for *ῥωσις*:—1. Oxidation. 2. Refining. 3. Active principle. 4. Production of a violet colour. In his opinion the word means refining (by oxidation of the base metal of a gold alloy, leaving a surface of pure gold), for he conceives of this recipe as similar to those which define the preparation of the so-called "Royal Cement." He states that the fourth definition, *Production of a violet colour*, though in use with the later (third century) alchemists, is inapplicable here.

This paper will endeavour to show that *ῥωσις* means "the production of a violet colour," or bronze (in these papyri, as well as later), as indicated by the four following arguments:—

(a) Historically it is evident that the original artisan of our papyrus was a dyer in purple, for Papyrus X. ends with recipes for dyeing, and the writings of the pseudo-Democritus are prefaced by two careful recipes for dyeing in purple. Also the dyer evidently transferred his dyeing methods to his new business as a worker in metal, for many of the recipes for producing metals of a golden colour strikingly resemble the methods of dyeing. The meaning given last in M. Berthelot's list would, therefore, stand as a link between the early work shop with its purple dye, and the usage of the later alchemists.*

(b) The chemical significance of this recipe called *ῥωσις χρυσῶν* may be seen from a passage in the manual of Hiorns. This author states (p. 152), on the authority of Roberts-Austen, that there is in use in Japan a method for producing upon copper containing some gold (which gold is intentionally introduced into the copper for this purpose), a beautiful rich purple coat or patina. The bronzing or pickling solution contains:—

Verdigris	220 grains
Copper sulphate	540 grains
Water	1 gallon
Vinegar	5 drachms

The presence of a little gold heightens the effect, for, as Hiorns found, copper turns a brownish-red when boiled in this pickle, while copper containing gold becomes purple.

* If the expression "the preceding preparation" in Rx. 15 is really a citation of the recipe called *ῥωσις χρυσῶν* in Papyrus V. as Berthelot claims, the title of Rx. 15 "colouring gold," and the meaning "colouring violet" would be an additional bond between the two recipes, and therefore between the two papyri. See, however, the argument beyond).

The similarity between this pickle and that of Papyrus V. is significant. We have only to suppose that the workmen were dealing with alchemistic "gold," for which there are many recipes in Papyrus X., rather than with pure gold.

Hiorns states (p. 108) that a solution containing suspended copper hydroxide, and red oxide of iron, produces on copper dipped in it, after removal and heating and numerous repetitions, a violet tint; and that brass (p. 226) dipped in acetic acid solutions tends to give iridescent effects, and that it is possible to arrest the bronzing process at the point of iridescence, and preserve these colours by lacquering (p. 154).

We may conclude that the recipe of Papyrus V. is proper for producing upon cast copper or brass, iridescence; and upon copper containing gold a purple or violet tint; and further conclude that the title of this recipe in Papyrus V. may be translated, *colouring gold violet (with iridescence)*. It would be indeed strange if the Egyptians possessing such a recipe as that of Papyrus V. should have failed to catch the brilliant colours produced upon the copper-gold alloys (Rxs. 56, 87, &c.), which stood for gold in those days, and used it, as M. Berthelot supposes,* for refining only, or for Royal Cement.

(c) Pliny's use of the word *virus*. Pliny describes ("Hist. Nat.," xxxiii., 25) a remedy made from gold by melting it with salt and misy and again with salt and schist. The gold remains intact and the other material is the remedy.

M. Berthelot notes that the word *virus* (poison) is the literal translation of the Greek *ῥωσις*, which means rust or poison, whence comes the word *ῥωσις*, the title of the recipe in Papyrus V. He therefore attempts to show a close relation between this recipe and that of the papyrus, translating this passage "gives active principle to the substances heated with it" (Berthelot, "Collection des Anciens Alchimistes Grecs," I., 15). It is more likely that this passage indicates an attempt to connect all bright coloured substances with medicinal properties, just as the philosopher's stone was considered a universal remedy. The most evident connection between the word *virus* and the Greek *ῥωσις* is found in Chapter 23 of the same book of Pliny's "Historia Naturalis," the noted passage concerning electrum, which has been so often cited as evidence of Pliny's credulity. Pliny here states, following the English translation of the Bohn edition: "Native electrum has also the property of detecting poisons (*venena deprehendit*), for in such cases semicircles resembling the rainbow in appearance will form upon the surface of the goblet and emit a crackling noise like that of flame, thus giving a two-fold indication of the presence of poison." With the meaning *poison*, or *active principle* for *virus*, or *ῥωσις*, this passage in the "Historia Naturalis" appears absurd. But, as has already been pointed out, *ῥωσις* means violet (or purple) bronze, and was so used by the later alchemists. It may be possible that the original Greek word which Pliny translated *stridore* (crackling noise), was *ῥωσις* dative of *ῥωσις* and was mistaken by Pliny for *ῥωσις* (a noise). If this be true, the sense of the passage would be very clear. "Native electrum has also the property of taking a violet bronze, and in such cases semicircular iridescence resembling the rainbow in appearance will form upon the surface of the goblet (in calcibus) together with streaks of violet, like flame."

* Hiorns (p. 104) gives a Chinese recipe which he could not make succeed. The pickle consists of copper acetate, cinnabar, ammonium chloride, and alum. If Hiorns had read this in the language of the third century, alum would possibly have been minium, or red oxide of iron, and sal-ammoniac may have been soda, or (as it seems to the writer) more probably borax. (See Berthelot, "Introduction," pp. 30, 45, 237, 251; and Pliny, "Hist. Nat.," xxxi., 39, and xxxi., 46). From experiments in this laboratory, it has been found that this Chinese-alchemistic recipe, so interpreted, gives with sheet copper (if the sheet is heated "until the layer breaks," and then plunged into water) a beautiful reddish-pink colour with wavy greenish lines. Probably the Japanese recipe (*ante*), and the Chinese recipe as just given, owe their origin to Egyptian alchemy.

Here, then, in Pliny is no evidence of credulity, but a clear statement of this wonderful bronze. The passage reminds us strangely of the descriptions given by Hiorns and Roberts-Austen. Pliny, without understanding at all what he was transmitting to us by almost literal translation, here recorded the great discovery of Egyptian alchemists. These workmen, who started as dyers of the royal purple, had begun to produce a purple bronze upon gold. The dyer in purple had become a bronzer in purple. Later, Democritus ("Natural Questions," 4; and "To Leucippus," 5) speaks of this bronze as "crysocorail," shell of gold, just as bronzers now speak of the patina, and *lōs* means violet, as Zosimos dreams of the priest whom he named "Iov in the temple" ("Zosimos," Lesson I., 2).

(d) In the acme of European alchemy, in the thirteenth century, when, on account of the possibility of closely identifying the metals, colours were no longer considered exponents of the precious metals or the great desideratum, we find the pseudo-Albertus, the charlatan, ending his description of processes inherited by him from the Egyptian workshops with promises of the victory coming to the alchemist as the reward of patient toil; "the mass is changed into a very red stone, which philosophers call blood or purple, red coral, red sulphur." This thirteenth century praise of red and purple, the "Philosopher's Stone," unintelligible to "Albertus," was but an inheritance from the Egyptian dye and bronzing works where purple, the royal colour, was produced from gold, the royal metal; and purple was the tincture* of gold; and metals which could produce a bronze of purple, violet, iridescence or even red were considered gold or nearly gold.†

The thirteenth century alchemists carry their mysterious processes through the black and white and yellow of the early alchemists (Olympiodor, "Sacred Art," 37-40, and Berthelot, "Les Origines de l'Alchimie," p. 242), but in the *finale* give purple and violet as the highest attainment of the art; in the Japanese and Chinese bronzing works, these processes for the production of purple have been preserved, untouched by European alchemy and just as they came from Egypt, for the use of our bronzers of today.

With the meaning of "Iouis established, the recipe in Papyrus V. becomes a recipe for bronzing, and we can turn to Rx 15, to see what light our notions of bronzing will throw upon it. It is not very clear why the two expressions, "la préparation précédente" and "la préparation susdite" should refer back past Papyrus V. to Papyrus V., as M. Berthelot suggests. The "preceding preparation" is certainly given in Rx 14, entitled "Making the mixture for a preparation," which gives directions for preparing a white alloy, like "bell metal," of copper and tin. This is "Asem" (as in Rx. 8), which M. Berthelot has shown by abundant illustrations was confused with gold and called χρυσος λευκός (Berthelot, "Collection des Anciens Alchimistes Grecs," I., p. 31, Note 1). It would seem very reasonable that this white "asem" should be "the mixture (alloy) for a preparation" of gold by adding it to gold or to real asem or to copper, as in Rx. 6, 8, and 56, this being common alchemistic practice. But if the "gold" of Rx. 15 is the copper-tin alloy of the preceding paragraph, the pickle described in Rx. 15 would produce upon it a fine yellow bronze (Hiorns, p. 107).

* See Berthelot, "Collection des Anciens Alchimistes Grecs," I., p. 267, under the words "Trempe-teinture," for the different meanings of this word in use among the alchemists.

† M. Berthelot states that though the later alchemists worked with coloured glasses, no recipes for this kind of work are found in Papyrus X. This papyrus was probably written upon the discovery of brilliant and permanent metallic colours similar to purple dye. The discovery of the method for making red and purple glasses probably antedated this papyrus, and by the time of the Democritan writings, recipes for coloured glasses became important to the alchemists. One of the first recipes for making a red glass is described in alchemistic language in "Technical Treatises," v., 6 (Berthelot, "Traduction," p. 333-4), in which after making green, yellow, white, and blue glasses, by mixing and rubbing and other processes, as the climax a red "cinnabar" or "gold" is produced.

If it is to be understood that this alloy was first to be added to some gold, the bronze would probably be purple with iridescence, for a second Japanese recipe quoted from Roberts-Austen (Hiorns, p. 152), to be used upon copper containing some gold, contains exactly the ingredients of Rx. 15 with the addition of sulphur and nitre. M. Berthelot's supposition that this Rx. 15 and the one in Papyrus V. are similar to the recipes for Royal cement is inadequate to the case. Rx. 25 is much more exactly the Royal cement, as it contains no acid, and the process is conducted in closed vessels.

But Rx. 25 is entitled "Gold Varnish," which Royal cement really is, as Macquer describes it (Berthelot, "Introduction," p. 15). As this title is correct, so probably is that of Rx. 15 "Colouring Gold"—the colour being that for which gold was noted, purple with iridescence. But this supposition of M. Berthelot's would further involve the separation of the two Rx. 14 and 15, which is very improbable. The expression in Rx. 15, "vinegar left from the preparation of gold," would seem to indicate the "preparation" (of gold) "above mentioned" in the title of Rx. 14, and that this recipe was a continuation of that process, a continuation in this sense:—Rx. 14 describes the making of "Asem," which was confounded with gold not because of its colour, for this preparation is white (see note, *ante*), but because it acted like gold (especially when a little [ferment of] gold was added to it) in assuming permanent and brilliant bronzes, such as are formed on fine gold; then Rx. 15 shows how to produce these colours—yellow, violet, purple, or iridescence. The colour was the important thing. In just this alchemistic sense of the importance of colour, Mary the Jewess says (Olympiodor, "Sacred Art," 40): "Our lead is artificially black . . . common lead is fundamentally black." The property of blackness was a more essential thing than lead or silver, just as liquidity was considered an entity present most largely in lead and mercury. So Rx. 14 directs the formation of that alloy which could produce and hold the essential (*i.e.*, colour) of gold, if treated as immediately directed in Rx. 15.

Rx. 16.—Increasing Gold.

"To increase gold, take Thracian cadmium; make the mixture with caked cadmium or that of Gaul."

Rx. 17.—Imitation of Gold.

"Misy and sinope red, equal parts to one part of gold. After having put the gold into the furnace and it has become of a fine colour, cast upon it these two ingredients, and removing (the gold) allow it to cool, and the gold is doubled."

M. Berthelot thinks Rx. 17 is a continuation of Rx. 16, because he considers Rx. 16 incomplete, and that the separating title, "Imitation of Gold," is a later marginal commentary which has crept into the text. It is probable that Rx. 16 and 17 bear the same relation to each other as was pointed out for the couplet Rx. 14 and 15. The first recipe in each is complete in itself in that the mixture or increase has been accomplished, but the product "asem" is only potentially gold and the colouring follows in each case, because that was the original intention in forming the alloy in the first process. In the absence of textual evidence, the title, "Imitation of Gold," would not then be considered a gloss. The titles of the recipes seem to be singularly correct and suggestive (see *ante*). The original Greek was not numbered, and a modern compiler would probably have made a separated couplet of the two Rx. 14 and 15, and another of Rx. 16 and 17 to bring out the clear thought. Rx. 16 would give us a light-coloured alloy of gold, zinc, copper, and lead. Treated as directed in Rx. 17, with sulphates of iron and copper, and either red oxide of iron or minium at a temperature at which the bright colour of gold and brass had begun to appear, copper would bronze a brown or red colour (depending on temperature and time), as we know from the results of similar recipes

given by Hiorns (Pp. 98-101). But the presence of the other metals would vary the effect, which would tend, as far as the influence of the gold was concerned, towards purple, as has been already pointed out.

The position taken in reference to these two recipes (16 and 17), is confirmed by Rxs. 87 and 88, which are practical copies of Rxs. 16 and 17. The first (Rx. 87) is called "Doubling Gold," and begins "To increase the weight of the gold." The second (Rx. 88) begins "One alters gold, on increasing it, with misy . . . &c." and ends "The gold is doubled." Then Rx. 89 follows with another method of bronzing, quite different from the method of Rx. 88.*

Rx. 36.—*Making Asem Black like Obsidian.*

"Asem two parts, lead four parts. Put in an empty earthen vase. Throw on it a triple weight of raw sulphur, and having put it in the furnace, melt. And having taken from the furnace, make a casting and form what you wish. If you wish to make an image in metal stamped or moulded, then polish and engrave. It does not rust."

Rx. 49.—*Gilding Silver.*

"In order to gild, without (gold) leaves, a silver or copper vase, dissolve some yellow soda and some salt in water. Rub with this, and it will be gilded."

Rx. 89.—*Another (process).*

"Invention of sulphur water (or holy water). A handful of lime and as much sulphur in fine powder. Put them in a vase containing strong vinegar or the urine of a young child. Heat from below until the supernatant liquid appears like blood. Decant the latter carefully to separate it from deposit and use."

Rx. 36 shows the importance attached to black. Black was the origin of all colours. Liquidity was the origin of all solids. Lead which was black and easily liquefied was at first the elementary metal until mercury supplanted it. Silver from its black bronze was allied to lead. (Olympiodor, "Sacred Art," 38). Asem was like silver or like gold either by its original white or yellow colour, or by its bronze, black, or purple. In the case of Rx. 36 we have a substance bronzed black, not on the surface only, but black through and through. It would not rust. It had a permanent colour. It was better than "oxidised silver." Rxs. 49 and 89 involve the use of soluble sulphides. M. Berthelot has shown that "yellow soda" is probably sulphide of soda, but characterises the recipe as obscure. The following quotation from Hiorns (p. 266), will remove this obscurity.

"The following is a most valuable solution for colouring silver goods:—

Barium sulphide	..	..	5 grains
Water	..	..	5 fluid ounces

This solution imparts a beautiful golden tint to silver, and when worked cold, almost any desired shade from pale to deep gold may be obtained according to the time of immersion. If the immersion is continued, the gold colour passes through crimson-purple to brown, the former being more or less iridescent. . . . To produce the gold colours, it is best to work with a cold solution, because the changes succeed each other more slowly, and the process can be stopped when the desired shade of colour is obtained."

Here we have white silver passing through the yellow colour of gold and on to crimson-purple with iridescence. First silver, then gold, last the "coral of gold." This was the highest of colours—the *ids*.

Rx. 89 gives the method for making "oxidised silver" by the use of a solution of soluble sulphide, stronger than the very dilute solution of Rx. 49. This recipe follows

* Perhaps Rxs. 87, 88, and 89 should be in a separate group and the titles of Rxs. 88 and 89 translated by Berthelot "*Antre*," and "*Antre*" would indicate what we would express by such an expression as: After Rx. 87, choose either of the two following elective processes. (See beyond for Rx. 89).

Rx. 88, which has already been shown to describe a bronzing process.

Rx. 64.—*Test for Asem.*

"To tell whether asem is counterfeit. Place in brine, heat; if it is counterfeit, it blackens."

In the case of this recipe the apparent obscurity is removed by a reference to Hiorns. He directs (p. 124). "Dissolve the copper chloride in the water, raise to the boiling-point, and immerse the previously well-cleaned copper articles for a few minutes. If the copper is pure or nearly pure, a very beautiful rich reddish-brown colour will be obtained, but with ordinary commercial copper containing 1 to 2 per cent of impurities the colour obtained is nearly black."

This was, therefore, a test for the foreign metals (other than tin) associated with copper, depending upon the production of the clear brown bronze characteristic of copper.

M. Berthelot has marked this recipe obscure, with nearly all the other recipes which have any alliance with bronzing methods. But by regarding the Egyptian artisan of these papyri as a bronzer, by accepting the fact that gold and silver were identified not only by the colour of the metals but also by the colour of the bronze they were capable of taking, the recipe given becomes at once clear.

In final justification of the two theses this paper has endeavoured to assert, many of the remaining recipes of Papyrus X., read from this changed point of view, become plainer and represent intelligent and workmanlike directions for producing either alloys capable of bright bronzes or bronzing solutions into which these alloys were to be dipped.

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RESEARCHES ON THE PRESSURE FORCES OF LIGHT.*

By PETER LEBEDEV.

(Continued from p. 40).

III. The Experiments.

THE methods described above allow two fundamental questions to be answered experimentally:—

- Whether light radiation can exert forces which are independent of the known secondary (conductive and radiometer) forces, and
- Whether these "weight moving" forces of light correspond to the pressure forces calculated by Maxwell and Bartoli.

Before the beginning of the experiment an auxiliary thermo-element (which was connected with a d'Arsonval's galvanometer) was moved along the direction of the axes of both lenses L_1 and L_2 (Fig. 1), and their focal lengths for the principal ray observed. Then the mirrors and the lenses of the apparatus (Fig. 1) were so adjusted that the real images of the diaphragm formed by the rays coming from the right and from the left fell at the same place.

In order to compare the intensity of both beams of light the thermo-element was placed where the real images were formed, and alternately illuminated from right and left. Usually only a small difference (scarcely reaching 1 per cent) was found in a great number of experiments; in the case of most reflecting glass surfaces an unequal distribution of dust is sufficient to account for such a difference.

If the thermo-element is moved ± 0.5 c.m. from its original position in the direction of the axis of the cone of light, the light-intensity diminishes for both directions

* From the *Annalen der Physik*, 1901, vol. vii., p. 433.

TABLE I.

Apparatus III. Platinised Vane (2). Distance of Centre of Disc from Axis of Rotation $\alpha = 9.2$ m.m.
Cooled with Ice and Salt. Distance of Scale A = 1195 div.

R. Calc.	L. Calc.	R. Calc.	L. Calc.	R.
176 240 306	115 206 295	184 245 307	174 210 244	—
239 302	118 207	244 303	177 211	—
177 239	208 296	184 243	212 245	—
240 302	124 209	243 300	180 213	—
178	294	189	247	—
240	208	244	212	—
Deviation 32 div.	36 div.	32 div.	—	—
Gb.	Gn.	Gb.	Gn.	Gb.
308		314		—
305		312		—
312	201	314	201	—
314		316		—
310		314		—
Galv. 109 div.	113 div.	113 div.		
Red. def. (G = 100) .. 29.3 div.	31.8 div.	28.3 div.		

In this Table—

R and L denote the turning points on the scale if the light falls from right (R) or left (L).

"Calc." in the middle column gives the position of rest calculated from three adjacent turning points.

"Deflection" gives the deflections of the system if the light is changed from right to left.

Gb and Gn give the positions of the galvanometer if the thermopile is illuminated or not respectively (galvanometer zero-point).

Galv. gives the galvanometer deflections.

Red. def. (G = 100) are the above named deflections reduced to a constant galvanometer deflection of 100 div.

of the rays by about 5 per cent. The preliminary investigations described are absolutely necessary.

The vane apparatus was so suspended that the rays coming from the lamp, which were reflected from the concave glass wall of the globe, could not illuminate parts of the vane apparatus.

After the vane apparatus was suspended the globe was closed, and for several days highly exhausted, heat being gently applied at the last to the whole glass covering, the single vanes being illuminated. Before each series of experiments the lower part of the globe containing the mercury was warmed in the water-bath to about 5° C. above the temperature of the room,* exhausted for one to two hours, then closed by the mercury in v (Fig. 5), and cooled by a mixture of ice and salt.

The chief error of the measurements is caused by disturbances originating in convection; these disturbances show themselves in constant movements of the zero-point, the magnitude and direction of which depend on accidental circumstances;† however, they are fairly small during the taking of one measurement, and may be eliminated by a long series of observations; convection of the residuum of mercury vapour is brought about both by the warming of the illuminated vane and by unequal warming of the walls of the globe, and especially by temperature differences of the two mercury surfaces. If an attempt is made to take observations without cooling the mercury considerable‡ disturbances appear owing to convection; these become much smaller when a freezing mixture is applied.

Another source of error lies in the inconstancy of the source of light;§ sudden fluctuations of the light-intensity

cause the amplitude of oscillation of the vane apparatus to alter by leaps and bounds; they can only be avoided by taking many observations.

The observer could alternately read off the vane apparatus and the galvanometer through two conveniently placed telescopes; an assistant who attended to the arc lamp could shift the mirrors s_1 , s_4 (Fig. 4) at bidding. By intermittent illumination the amplitude of oscillation of the vane apparatus could be brought to any desired magnitude.

Table I. gives the commencement of a record of observations.

As shown in Table I. seven R and L observations were taken for each vane, and the "def. red." obtained were united to a mean specifying the mean $\pm$ divergence of all observations from that mean. (For the vane of Table I. the double deviation = 29.4 ± 1.6 div.).

In order to be able to compare the measurements, which were made with individual discs, more easily at sight, certain calculations and corrections are necessary.

In the apparatus I. and III. a band of light (breadth about 3 m.m.) falls on the supporting arms, and this increases the deflection. By measuring the illuminated parts and their axis distance this amount, which in different vanes varies from 5 to 10 per cent, may be calculated and deducted; thus we get the deflection brought about by the circular discs alone. (Apparatus II. does not need this correction). For the vane of Table I. this correction amounts to 1.9 div.; the calculated double deflection would be 27.5 div.

The measurements of the distances of the mid-points of the discs from the axis of rotation were accomplished as follows:—The mirror apparatus (Fig. 1) was drawn back on the sliding base, a plumb line of thin silver wire was hung close in front of the globe on the side of the incident light, a telescope was placed perpendicular to the vane arms about 4 m.m. away, and the wire moved until it appeared to coincide with the torsion thread. The telescope had a micrometer eye-piece, which was read by the help of a scale placed close to the globe; the apparent distance of the disc centre from the silver wire, which

* With this small temperature difference no mercury is deposited on the colder parts of the apparatus, a phenomenon which was pointed out by M. Cantor in the case of surfaces not capable of being moistened.

† In researches with the same vane on different days the magnitude and direction of the deviations of the zero point could appear very different.

‡ At higher pressures the observations are rendered very uncertain by convection, and scarcely admit of reliable measurements.

§ Siemens's "A Carbons" have proved very good; with inferior carbons it is scarcely possible to take measurements.

corresponds to the true distance of the axis of rotation, could be exactly observed to 0.5 m.m. The magnitude of these distances lay between 9 and 11 m.m.

On the basis of these measurements the observed deflections were reduced to a deflection corresponding to an axis distance of 1 c.m. For the vane of Table I. the reduced double deflection amounts to 29.9 div.

In order to express in absolute measure the magnitude of the observed pressure which the light exercises on the vane under examination, a measurement of the direction force of the suspension thread was taken by means of observations of the oscillations, while the periods of oscillation were obtained from three series of observations of ten oscillations.

TABLE II.

Half oscillation period.	Inertia body. Copper-wire.
Mirror alone .. $\frac{t_1}{2} = 5.1 \pm 0.05$ sec.	Length = 4 c.m.
Mirror + inertia body .. $\frac{t_2}{2} = 29.4 \pm 0.1$ sec.	Mass = 0.314 grm.

Direction force $D = 0.00494$ dynes.

Based on this direction force we obtain for the vane of Table I. the magnitude of the pressure for partial illumination expressed in dynes—

$$p = 0.0000308 \text{ dynes} \pm 0.0000007 \text{ dynes.}$$

In order to prove the relation stated by Maxwell and Bartoli we must calculate the pressure forces which the light radiation of the experiments must exert according to Maxwell and Bartoli, and this calculation must then be compared with the result of the experiments. For this a calorimetric measure of energy and a photometric determination of the reflecting power are necessary.

(To be continued.)

EXPERIMENTS RELATIVE TO THE CONSTITUTION OF PECTOLITE, PYROPHYLLITE, CALAMINE, AND ANALCITE.*

By F. W. CLARKE and GEORGE STEIGER.

(Continued from p. 47).

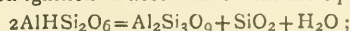
Pyrophyllite.

THE empirical formula for pyrophyllite, AlHSi_2O_6 , is apparently that of an acid metasilicate, and the mineral is therefore peculiarly available for fractional analysis. The compact variety from Deep River, North Carolina, was taken for examination, and a uniform sample was prepared. Analysis gave the following results:—

SiO_2	..	..	..	..	..	..	..	64.73
TiO_2	..	..	..	..	..	..	..	0.73
Al_2O_3	..	..	..	..	..	..	..	29.16
Fe_2O_3	..	..	..	..	..	..	..	0.49
MgO	..	..	..	..	..	..	..	trace
Ignition..	..	..	..	..	..	..	..	5.35

100.46

If, now, pyrophyllite is an acid metasilicate it should break up on ignition in accordance with the equation—



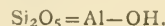
that is, one-fourth of the silica, or 16.18 per cent, should be liberated. The mineral itself is very slightly attacked by boiling with the sodium carbonate solution, and in an experiment of this kind only 0.72 per cent of silica was dissolved. Upon ignition under varying circumstances the following data were obtained:—

Ignited ten minutes over a Bunsen burner, and then extracted with sodium carbonate solution, 1.51 per cent of SiO_2 dissolved.

Ignited fifteen minutes over a Bunsen burner, 1.89 per cent became soluble.

Ignited ten minutes over a Bunsen burner and then fifteen minutes over the blast, 2.84 per cent of silica was liberated.

These results are of a different order from those given by pectolite and talc, and raise the question whether pyrophyllite, despite its ratios, is a metasilicate at all. So far as the evidence goes, it may with propriety be regarded as a basic salt of the acid $\text{H}_2\text{Si}_2\text{O}_5$, and its formula then becomes—



This formula is at least as probable as the metasilicate expression, which latter rests upon assumption alone. Still other formulæ, but of greater complexity, are possible; but until we know more of the genesis and chemical relationships of pyrophyllite, speculation concerning them would be unprofitable.

By heating with dry ammonium chloride, pyrophyllite is very slightly attacked. In two experiments it lost in weight 6.17 and 6.30 per cent respectively. The excess of loss over water is due, as we have proved, to the volatilisation of a little ferric and aluminic chloride. The residue of the mineral after this treatment contained no chlorine, so that no chlorhydrin-like body had been formed. The formation of such a compound, the replacement of hydroxyl by chlorine, would, if it could be effected, be a valuable datum toward determining the actual constitution of the species.

Calamine.

The simplest constitutional formula for calamine, the one which is generally accepted, represents it as a basic metasilicate, $\text{SiO}_3 = (\text{ZnOH})_2$. In this the hydrogen is all combined in one way, and so, too, is the zinc. In all other possible formulæ, simple or complex, the hydrogen as well as the zinc must be represented as present in at least two modes of combination; a condition of which, if it exists, some evidence should be attainable. Our experiments upon calamine have had this point in view; and we have sought to ascertain whether water or zinc could be split off in separately recognisable fractions. Our results, in the main, have been negative, and tend toward the support of the usual formula; but the data are not conclusive, although they seem to be worthy of record.

The beautiful white calamine from Franklin furnace, New Jersey, was selected for study, and gave the subjoined composition:—

Analysis.								
SiO_2	..	..	..	..	..	..	..	24.15
Al_2O_3	..	..	..	..	..	..	..	0.19
ZnO	..	..	..	..	..	..	..	67.55
CaO	..	..	..	..	..	..	..	0.12
H_2O	..	..	..	..	..	..	..	7.95
								99.96

Fractional Water.								
At 100°	..	..	..	..	..	..	..	0.27
At 180°	..	..	..	..	..	..	..	0.22
At 250°	..	..	..	..	..	..	..	0.75
At 300°	..	..	..	..	..	..	..	0.88
Incipient red heat	..	..	..	..	..	..	..	4.46
Full red heat	..	..	..	..	..	..	..	1.37
								7.95

Here no clear and definite fractionation of the water is recognisable, at least of such a character as to suggest any other than the ordinary formula for calamine.

Upon boiling powdered calamine with water practically nothing went into solution, but by boiling with the solution of sodium carbonate 0.25 per cent of silica was dissolved. After ignition at a red heat, only 0.14 per cent of

* Bulletin of the United States Geological Survey, No. 167.

silica became soluble in sodium carbonate, and after blasting, only 0.24. In these experiments a very little zinc was dissolved also; but there was no evidence that any breaking up of the mineral into distinguishable fractions had occurred. In a hot 10 per cent solution of caustic soda both the fresh and the ignited calamine dissolve almost completely; but boiling with aqueous ammonia seems to leave the mineral practically unattacked. All experiments aiming to extract a definite fraction of zinc while leaving a similar fraction behind resulted negatively.

By heating with dry ammonium chloride, calamine is vigorously attacked, and gains in weight by absorption of chlorine. In two experiments the mineral was intimately mixed with three times its weight of powdered sal-ammoniac and heated in an air-bath for several hours to a temperature somewhat over 400°. A large part of the residue was soluble in water, and the percentage of this portion, together with the percentage increase in weight, is given below.

	I.	II.
Gain in weight	27.60	25.78
Soluble in water.. ..	53.23	67.13

A conversion of calamine into the chlorhydrin, $\text{SiO}_3(\text{ZnCl})_2$, would involve a gain in weight of 15.34 per cent. Complete conversion into $2\text{ZnCl}_2 + \text{SiO}_2$ implies an increase of 38.14 per cent. The figures given lie between these two; and are indefinite also for the reason that there was volatilisation of zinc chloride.

In two more experiments the calamine, mingled with three times and four times its weight of ammonium chloride respectively, was heated for an hour and a half to bright redness in a combustion tube. The zinc chloride which was formed volatilised, and was collected by suitable means for determination. It corresponded to 59.6 and 59.0 per cent of the original mineral, calculated as zinc oxide; which indicates a nearly complete decomposition of the calamine into $2\text{ZnCl}_2 + \text{SiO}_2$. The residue was mainly silica, with a small part of the zinc, about half of the silica being soluble in sodium carbonate solution. Here, again, no definite fractionation of the mineral could be observed.

Finally, the action of dry hydrogen sulphide upon calamine was investigated. The mineral was heated to redness in a current of the gas, and gained perceptibly in weight. The percentage data, reckoned on the original calamine, were as follows, in two experiments:—

	I.	II.
Gain in weight	6.00	6.43
SiO_2 soluble in Na_2CO_3 ..	16.45	20.95
Sulphur in residue	—	24.12

Complete conversion of calamine into $2\text{ZnS} + \text{SiO}_2$ implies a gain in weight of 5.80 per cent; and it is therefore evident from the figures of the second experiment that the limit of change was approached very nearly. The 24.12 of sulphur taken up is quite close to the 26.53 per cent which is required by theory. About eight-ninths of the calamine had undergone complete transformation. Again, no definite fractionation was detected.

The hydrogen sulphide reaction was examined still further with reference to the temperature at which it becomes effective. Even in the cold calamine is slightly attacked by the gas, but its action is unimportant until the temperature of 400° is approximated. Then it becomes vigorous and the reaction goes on rapidly. A few experiments with willemite showed that it also was attacked by hydrogen sulphide, but less vigorously than calamine.

(To be continued).

The Sanitary Institute.—A donation of one hundred guineas has been made by the Vinolia Company to the Fund for the new Building and Endowment of the Parkes Museum.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1902.

Prof. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

MESSRS. Jollyman, Kettle, and J. H. Allworthy were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edwin Bayles Atkinson, Scartho House, Great Grimsby; Matthew Bradbury Challen, Daylesford, Victoria; Noël Heaton, 20, Girdlers Road, West Kensington, W.; William Brannan Jackson, Glengowan, Caldercruix, N.B.; Selwyn Philip James Levelle, Royston Villa, Ashby Road, Burton-on-Trent; Allan Ogilvie, 19, Market Street, Millom, Cumberland; Nevil Vincent Sidgwick, Lincoln College, Oxford; James Swain, 17, Winsham Street, West Side, Clapham Common, S.W.

Day and Hour of Meeting.

The Council has decided, on the recommendation of the Committee appointed for the purpose, that for the remainder of the Session the Ordinary Meetings of the Society shall be held at the following times:—

January: Thursday, Jan. 16, at 8 p.m.
February: Thursday, Feb. 6, at 8 p.m.; Wednesday, Feb. 19, at 5.30 p.m.
March: Thursday, March 6, at 8 p.m.; Wednesday, March 19, at 5.30 p.m.
April: Thursday, April 17, at 8 p.m.; Wednesday, April 30, at 5.30 p.m.
May: Thursday, May 15, at 8 p.m.; Wednesday, May 28, at 5.30 p.m.
June: Thursday, June 5, at 8 p.m.; Wednesday, June 18, at 5.30 p.m.
Annual General Meeting, Wednesday, March 26th, at 4.30 p.m.

Of the following papers, those marked * were read:—

*1. "An Investigation of the Radioactive Emanation produced by Thorium Compounds." I. By E. RUTHERFORD, M.A., D.Sc., and F. SODDY, B.A.

The main questions examined by the authors are:—(1) Can thorium, the emanating power of which has been largely destroyed by ignition, have this property restored to it by chemical treatment? (2) Is emanating power to be regarded as a specific property of thorium, or is it due to the presence of a foreign material? (3) Does the radioactive emanation itself resemble in chemical nature any known substance?

The electrical methods employed for the measurement of emanating power and radioactivity depend on the universal property of the radiations from substances known as radioactive of ionising or producing charged carriers from the gas through which they pass whereby the gas is rendered capable of conducting a current of electricity. The amount of the current, measured by means of a quadrant electrometer, affords the means of comparing the intensities of radiations, and the method is capable of a degree of precision and rapidity impossible with the better known photographic method. Use was made of the rate of decay of the radiation from the emanation with lapse of time to recognise and distinguish between different types of emanation, and the study of the phenomena is thus rendered qualitative as well as quantitative in character. The means employed for eliminating the effects of the emanation from the effects of the straight line radiation and *vice versa* were explained.

The first question is conclusively answered in the affirmative. After solution and re-precipitation, no difference was observed in the emanating powers of thorium compounds prepared from ordinary thorium, and thorium de-emanated as

completely as possible by intense ignition. The latter process must therefore be regarded as an obliteration of the effect rather than a removal of the cause. The emanation of thorium by ignition leaves the straight line radioactivity quite unaffected.

With regard to the second question, the attempts first made to separate from thorium a substance to which the emanating power could be traced were not successful. These included a fractionation of the sulphate and a precipitation of thorium by potassium azoimide according to the method of Dennis. No change in either the emanating power or radioactivity was observed in thorium prepared by these methods. Subsequently, results of a different character were obtained.

It was found that water vapour increases, and desiccation decreases the normal value of the emanating power, the extremes varying in the ratio of 2 to 1. Cooling acts powerfully in the opposite direction to increase of temperature. At -78° , the emanating power was only one-tenth of the normal, but no permanent alteration in value is produced. The lapse of time in increasing the emanating power of freshly prepared thorium hydroxide is very striking. A maximum value appears to be attained after some days, and this is not much affected by sealing up the substance in glass.

An investigation of the third point, the chemical nature of the emanation itself, showed that this possesses the property of chemical inertness which characterises the members of the argon family. Using in the different cases suitable gases to carry the emanation from the thorium, it was subjected to the action of the following reagents on its way to the testing apparatus:—Red-hot lead chromate, white-hot platinum, platinum-black raised gradually to a white heat, red-hot magnesium, zinc dust, and palladium black. In each case the radioactivity of the gas current was quite unaffected, proving that, not only is the emanation not absorbed by these reagents, but also that its radioactivity is not thereby affected. The possible explanation that the emanation is the manifestation of excited radioactivity on the surrounding atmosphere was shown to be untenable by a crucial experiment. Since the only known gases which would survive in unaltered amount the action of all the reagents employed are the gases of the argon family, the authors conclude that the emanation is allied in properties to the elements of this group.

The emanating power of thorium nitrate, which in the solid state is only 1.8 per cent of that of thorium, is increased 200 times by solution in water. It was also found that the emanating power of the carbonate varies enormously with the method of preparation, and specimens of it have been obtained differing in the ratio of 80 to 1, of which the highest possesses four times the value of thorium.

A remarkable observation has been made on the solutions from which thorium has been precipitated with ammonia; although these should be free from thorium, they still possess both emanating power and radioactivity in considerable amounts. This has led to the preparation of substances free from thorium, but possessing radioactivity and emanating power indistinguishable from that of thorium, many hundred, in some cases over a thousand, times as active. The identity extended to the penetration power of the rays for metals and the rate of decay of the emanation. The fact that those processes in which a portion of the emanating material is certainly removed from thorium does not much affect the value of the emanating power of the latter, taken in conjunction with the very great variations which this value suffers in different circumstances and often spontaneously with time, leads to the belief that emanating power is the manifestation of a dynamical change rather than a function of matter in the static condition. In the same way as in chemical reaction, the active mass of a reacting solid appears independent of its quantity, so the rate of the change, of which emanating power is a measure, does not

depend solely or even mainly on the quantity of emanating material present. The removal of the latter is consequently not accompanied by corresponding changes in the emanating power. The straight line radioactivity, on the other hand, is apparently unaffected by any of the causes which so profoundly alter the value of the emanating power, and appears much more likely to be additive with regard to mass. The effect of the removal of an intensely radioactive and emanating material from thorium is found, in accordance with this view, to reduce the straight line radioactivity of the thorium very materially. These results show that thorium is partially separated from ThX, the constituent responsible for its activity, and the latter can be obtained free from thorium.

The chemical examination of the thorium-free active substances prepared in the manner described showed the presence of an unknown substance, precipitated from its solutions by sodium phosphate. This the authors regard as merely an accidental impurity. The actual ThX is probably present only in minute quantity, exhibiting the behaviour of being dragged down by precipitates, without reference to its true analytical behaviour.

Another method of separation confirms this view. By evaporation of water with which thorium has been shaken for some time, small deposits are obtained which are often of the order of a thousand-fold more active than the original thorium. The washed sample exhibits a considerable reduction of radioactivity after the process, whilst the character of the radiations as before is identical with the ordinary thorium radiation. A careful chemical examination failed to reveal the presence of any other element besides thorium. The view that the radioactivity and emanating power of thorium is to be ascribed to the presence of a minute amount of a constituent ThX of correspondingly great activity is thus confirmed.

DISCUSSION.

Mr. VERNON HARCOURT had previously read two papers by Professor Rutherford in the *Philosophical Magazine* which explained the apparatus used by the authors. The authors' conclusion that the influence upon the conducting power of air or other gas interposed between oppositely electrified surfaces is due, not to an imponderable force radiating from the molecules of thorium, but to the escape in minute quantity of some substance which is mixed with the thorium, and which can be dissolved and precipitated, was of very great interest. He might recall the observations and conclusions of Dr. Russell, who had investigated the photographic effect of the emanation from a number of substances, and had similarly concluded that the results were due, not to such an agent as light or electricity, but to the action of hydrogen peroxide.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, January 24th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

A PAPER ON "The Factors of Heat" was read by Mr. JAMES SWINEBURNE.

In all branches of physics, except heat, energy is divided into pairs of factors. Heat is generally thought of as a sort of indivisible energy and is not split into factors, but is treated as a whole, so that we have conductivity for heat, capacity for heat, specific heat, &c. Capacity for heat and specific heat are also taken when they include external work, at constant pressure for instance; so that the capacity is reckoned as capacity for energy which is only partly in the body or substance. So little is heat realised as energy that it has its own unit, so that equations involving other forms of energy with it need to be complicated with a coefficient. Temperature might be a factor of heat; but there is no corresponding quantity

factor. There is no unit of temperature; it is measured in degrees which have no proper connection with anything. Temperature is sometimes treated as a tension factor with heat as the quantity factor, as when heat is said to run down temperature. Heat is thus regarded as its own quantity factor. Entropy is sometimes incorrectly used as the quantity factor corresponding to temperature. Entropy is at present indispensable as a function involving information as to whether heat has been, or might have been, converted into work. The author discusses "chy" as a possible factor for use with absolute temperature where "chy" is a quantity factor, such that when multiplied by the temperature at which it is added or withdrawn gives the energy added or withdrawn. In the θ, x system capacity, specific capacity and conductivity vary inversely as the temperature. These factors are not analogous with the factors of other forms of energy, and are not convenient. The energy of heat is therefore split into $\tau\pi$, where τ is proportional to the square root of the temperature, and is called by the author "tasis." The other factor, π , is called "posot." In any gas, tasis is proportional to the effective velocity and posot to the momentum. Tasis and posot are analogous to the tension and quantity factors already in successful use and indispensable in the treatment of other forms of energy. Conductivity of posot follows Ohm's law, and the capacity of a body for posot is constant.

Prof. EVERETT said the author of the paper had made a bold attempt to put the theory of heat on a better foundation. One objection to his proposals was that the two new variables, tasis and posot, were not independent, at all events in dealing with a perfect gas. The energy of the gas being $\frac{1}{2}mv^2$, tasis was represented by v and posot by mv . There was thus only one independent variable (for m is a constant mass), and arbitrary variations in the condition of the gas could not be represented. Another objection was the dubious nature of posot. Posot was described as momentum; but the total momentum of the gas was zero; its centre of gravity being at rest. Momentum as a determining element in physical phenomena was always a vector, and yet posot was a scalar. It was not even the mass multiplied by the arithmetical average of velocity; for v was not the average of velocities, but the velocity of mean square. The claimed simplification of the law of conduction rested on the erroneous assumption that the conductivity of a metal is inversely as its absolute temperature. He thought the proposed changes involved loss of simplicity without compensating advantage, and had been suggested by an undue desire to imitate electrical methods in the treatment of heat.

The SECRETARY read a letter from Prof. G. H. BRYAN, in which he said that the author's system was very difficult to understand from his paper, but when reduced to its simplest terms it appeared to possess great disadvantages in comparison with the conventional method of thermodynamics. Mr. Swinburne's proposal to put $dU = Tdx$, where x is what he calls "chy," had the disadvantage that dx was not a perfect differential, and the value of x for any body depended not only on its actual state but also on its past history. The same thing occurred when tasis and posot were used, as $d\pi$ was not a perfect differential, and the two quantities seemed more inconvenient than chy. The paper overlooked points of vital importance, and contained a great deal of irrelevant matter about stand-pipes and reservoirs. It would be interesting to know whether the heat element, dQ (not the total variation of energy, dU , used in the paper in defining tasis and posot), could be put into the form $q'dp$ where q' is of the dimensions of the velocity, and dp of the dimensions of momentum.

Dr. DONNAN said that Mr. Swinburne's objections to entropy as a factor of heat energy seemed, at any rate as far as reversible operations were concerned, to be based either on a misconception, or on some novel conception of the real significance of such factors. All that was

really known was that the "actions" of the external world on a given system could be expressed, in reversible thermodynamics, by differential terms of the form idm , where i and m were parameters of the system. In general, the separate terms were not perfect differentials, and the futility of an attempt to give a false reality to what were merely mathematical functions suitable under certain conditions had been pointed out by Planck. The suggestion to replace temperature by its square root so as to bring heat energy into line with electrical and kinetic energy had already been made by Mach. In dealing with irreversible actions the author claimed that the phenomena of heat conduction could be represented as a flux of posot along a down gradient of tasis according to the same law as a flux of quantity of electricity along a down gradient of potential. He pointed out that it was not necessary to abandon entropy to achieve this result, as Wiedeburg had shown that by making some very simple and plausible assumptions it was possible to bring entropy into line with other quantity factors, so that the entropy of a heat-isolated system remained constant, and the flow of heat could be represented as an entropy flux obeying a law analogous to that of Ohm.

Mr. MACFARLANE GRAY said that he had found the paper difficult to understand. Such expressions as:—"But the gas has increased its entropy by H/θ collected in the gas, and caught there," "the gas loses entropy," "a flow of entropy," were strange to him, his idea being that there is no entropy in any substance or in nature, neither is it a property or a quality of any body, but only length upon a diagrammatical representation of the related heat states of a body of unit mass, according to a systematised mental conception. He thought temperature and entropy were sufficient for this purpose, and he could see no advantage in the factors proposed. From certain statements in the paper he had concluded that chy was the specific heat of the working substance, but there were other statements inconsistent with this conclusion. He had, with what he had taken tasis to be, constructed a diagram to ascertain how the system proposed differed from the θ, ϕ , method. Starting with tasis proportional to the square root of the temperature he had not inquired what posot might be, because with heat energy and one ordinate fixed the other would declare itself. On this new diagram a graph is not a series of state points, and a cycle performed thermodynamically is not a closed curve. In the vapour field the adiabatics are sloped curves, and the dryness fraction is measured in the same way as on the old diagram. In the gas field he had set out problems similar to the illustrations in the paper, and found that the features were the same, so that he thought he had operated with the same "posot," although undisclosed.

Mr. SWINBURNE, in reply to Prof. Everett, said that τ and π were only proportional when the capacity was constant. The factors proposed were not only analogous to those used in electricity, but also to those used in other branches of physics. Prof. Bryan had discussed what ought to come in a subsequent paper, and evidently thought the subject should be commenced by dealing with generalised co-ordinates, whereas he (the author) had started simply, and on that account had used stand-pipes and perfect gases as illustrations. He remarked that although some members had found the paper difficult to follow, others had complained that it was too simple.

Mr. EUSTACE LARGE then exhibited some Twinned Crystals of Selenite, and the Society adjourned until February 14th.

Amylic Alcohol Formed during Fermentation.—G. Bemont.—Amylic alcohol formed during fermentation boils at 131° . It gives, on oxidation, an active valeric acid boiling at 175° , which seems to be the methyl-ethyl-acetic acid. It probably only contains a little isopropyl-acetic acid.—*Comptes Rendus*, cxxxiii., No. 26.

NOTICES OF BOOKS.

Répertoire Général ou Dictionnaire Méthodique de Bibliographie des Industries Tinctoriales et des Industries annexes. Depuis les Origines jusqu'à la fin de l'Année 1896. *Technologie et Chimie.* Par JULES GARÇON. Ouvrage honoré du Grand Prix Décennal DANIEL DOLLFUS, de la Société Industrielle de Mulhouse. Paris: Gauthier-Villars. 1900-1901. 3 vols. Roy. 8vo. Pp. 340 and 1638.

THE descriptive title of this great "Bibliography of Dyeing and Related Industries" explains its character, but fails to convey any idea of the immense labour required to compile it, or to show its arrangement of matter. The latter point is the object of this notice.

The work begins with a statement of the principles controlling the admission of items and their classification; incidentally, we note that the author gives an account of the decimal system of classification originating with Mr. Melvil Dewey (librarian of the Regents of the University, New York), and his reasons for rejecting the same. This introduction is followed by a chapter containing a list of the chemical bibliographies that have appeared in English, German, and French, and which serve as the sources of information used in this dictionary. The author gives the foremost place in chemical bibliography to Americans, and proves it by the long list of general and special works they have produced.

"Tableau I." contains a list of titles of subjects treated, in alphabetic order, from "Accidents" through "Mordants" to "Zinc." "Tableau II." contains a list of the periodicals that were examined in preparation of the second and third volumes; they number 110, and comprise about 5000 individual volumes. After a list of abbreviations (Tableau III.) there is a long list of the proper names cited, and this occupies 263 pages, double columns; to each name is attached the numbers of the pages where they may be found; in this section there are no less than thirty-six references to the names A. G. and W. H. Perkin, and a score or more to J. J. Hummel.

The 1600 pages following contain the references, arranged first under subjects alphabetically, and secondly, under each subject by the periodicals examined; this economises space and type, yet with the copious indices makes the use of the work very simple. The titles of independent works precede the periodicals under each subject. Patent literature is included. Bibliographically the work is accurate.

It does not often fall to the lot of a book-reviewer to discover in a work of this character the elements of romance; it is a pleasure to note that the author, in thanking persons who assisted him in preparing the volume, includes the name of the young lady who laboured for months at arranging the slips. And he naively adds "now M^{me}. Jules Garçon." He may be congratulated on the success of his enterprise in bibliography in at least two ways.

These volumes will be needed in the working libraries of all persons engaged in dyeing and colour-printing of textile fabrics, and they ought to be found for reference purposes in every public library. The three volumes are published at 100 francs. H.C.B.

Self-Examination for Medical Students. Third Edition, Enlarged. Philadelphia: P. Blakiston's Son and Co. 1901. Pp. 230.

THIS pocket-book contains 3500 questions on medical subjects arranged for self-examination. It also contains the proper references to standard works in which the correct replies will be found, as well as some examples of questions asked by the State Examining Boards of New York, Pennsylvania, and Illinois. As the practice of medicine is very much the same throughout the civilised world, this book will be useful to any English-speaking

student. By its help the student can successfully question himself on all the important branches, or coach himself on any one subject in which he feels himself to be deficient. As a rule the questions have been selected with regard to their bearing on practical medicine, but at the same time there are throughout the book many unusual ones, thus giving the user a wide range of thought. We can recommend this book as being likely to be of great assistance to medical students, who would certainly qualify with ease if they had mastered only a part of the questions put.

A Text-book of Urine Analysis for Students and Practitioners of Medicine. By JOHN H. LONG, M.S., D.Sc. With numerous Illustrations. Easton, Pa.: The Chemical Publishing Company. Pp. 249.

THE subject of practical urine analysis is treated in this volume in a concise manner, adapted to the requirements of medical students engaged in class-work, and also to the wants of the medical practitioner who has occasion to make more than the usual simple qualitative tests in urine examinations. A large number of quantitative methods are carefully described, and in such a manner that anyone with a previous training and experience in the manipulation of chemical apparatus should be able to follow them, while no doubtful methods have been included at all.

Numerous references are made throughout the text to the clinical significance of what is found by the various tests; and in the appendix a section is devoted to a tabular statement of the relation of pathological conditions to the chemical composition of the urine.

The book is divided into twelve chapters and an appendix; it is well and clearly printed and bound, and provided with a good index of ten columns. It should certainly be within the reach of, if not in the hands of, all medical students.

On the Composition of Dutch Butter. By Dr. J. J. L. VAN RYN. London: Baillière, Tindall, and Cox. 1902. Pp. 48.

IT has repeatedly happened, so the author tells us, that Dutch butter, the origin of which placed its genuineness and purity beyond doubt, has wrongly been declared by foreign (that is to say, not Dutch) chemists to be a mixture of butter and margarine. Great loss was suffered on this account, especially with regard to the English trade. The Dutch Government, therefore, caused a full examination to be made into the composition of Dutch butter produced in the latter months of the year, as it had been noticed that the difficulties arose almost exclusively in the course of each autumn. In order to become acquainted with the composition of Dutch butter, samples were analysed weekly from various parts of Holland, and particulars were collected under the following heads:—1. Number and breed of the cows from which the butter was obtained. 2. Age of the cows. 3. Date on which the cows last had a calf. 4. Approximate date of the next throwing of calf. 5. Nature of soil on which they grazed. 6. Nutrition. 7. Date of their being stabled.

The figures obtained by the examination of the butters have been arranged in order of time in twenty-five tables. These figures relate to refraction, specific weight, volatile acids, solid acids, dissoluble acids, saponification value, and iodine value.

From these figures it is seen that there are variations in the composition of the butters, and it was found that the rise in the percentage of volatile fatty acids begins shortly after the cows have been stabled. This is observed in all cases, and is very remarkable, because, until now, it has not been observed, or rather had escaped notice.

After describing a number of other experiments and generally discussing the question, the author states that he has established for a certainty that the abnormal chemical composition of Dutch butter during the autumn must be

attributed to the circumstance that the farmers leave their cattle in the meadows until late in the year, and he also claims to have proved that an earlier stabling prevents the calling into existence of the abnormal composition under discussion.

By "stabling," he points out, two varying factors are introduced; first, the cows are differently fed, and second, they are sheltered from the variations of weather and temperature. He has not, however, been able to decide with certainty whether both factors play an equal part, or whether one has a greater influence than the other.

Grundlinien der Anorganischen Chemie. By W. OSTWALD. Leipzig: Wilhelm Engelmann. 1900.

In a lengthy preface to this admirable book the author explains his reasons for modifying in some respects the usual arrangement and order adopted in a text-book of inorganic chemistry, and on following his system throughout the volume, we feel that he is fully justified in his conclusions. The book represents the work of a teacher thoroughly conversant with the requirements of the student, and also of the fellow teacher, though in a lesser and subordinate degree. Recognising that, for various reasons, it is not possible to employ the ideal method, and build up chemistry as a rational science on the basis of certain principles, introducing the description of the various substances simply in illustration of these general laws, the author has fallen back on the plan of fitting in to the detailed description of the elements and their compounds, as opportunity offers, the discussion of the general principles and laws underlying the science, and has met with marked success, in spite of the special difficulties with which he has had to cope in the use of such a method.

Briefly, the chief features of the book are the strictly logical sequence in which ideas new to the student are put forward, and the lucidity of the explanations of theoretical portions of the subject which usually present great difficulty to the learner. Since the book only professes to deal with pure chemistry, practical applications receive but little attention, and manufacturing processes are only very shortly described.

CORRESPONDENCE.

THE VOLUMETRIC ESTIMATION OF MANGANESE.

To the Editor of the Chemical News.

SIR,—We do not agree with Mr. Ramage's summing up of the issues between us; and with your permission we propose to make another and final attempt to show that for the general purposes of a steel works laboratory the use of ferrous sulphate is to be preferred to hydrogen peroxide.

The exception Mr. Ramage takes to the table of results published in our last letter, viz., "they are not of the high degree of accuracy established for our method," is an indication that he fails to grasp their significance. The figures obtained on the three steels by the bismuthate process as we prefer to work it were:—

0.31 1.01 0.89 per cent Mn.

The results obtained by separating the iron and manganese with acetate, &c., and finally making a bismuthate estimation (using hydrogen peroxide) on the pure manganese obtained from 2½ grms. of steel were:—

0.32 1.02 0.90 per cent Mn.

This latter process was devised out of regard for Mr. Ramage's distrust of any of the usual gravimetric processes, and we are prepared to take its indications as a standard. The variation between the two sets of figures just given is 0.01 per cent Mn. If one considers the

widely different means by which these two sets of figures were reached, and the facts that the titrations were made with different solutions (H_2O_2 and $FeSO_4$), and that different weights of material were operated upon, the 0.01 per cent differences are very inconsiderable. Will Mr. Ramage notice that *under the best possible conditions* the variation in his results is only 0.004 per cent Mn less than in ours?

The following results which were obtained on the same steel, after destroying organic matter in the hot solution, show the comparative effects of excesses of hydrogen peroxide and ferrous ammonium sulphate in the titration of the filtered permanganate solution:—

N/10 H_2O_2 used. C.c.	Mn obtained. Per cent.	N/10 $(NH_4)_2(SO_4)_2Fe$ used. C.c.	Mn obtained. Per cent.
5	0.497	5	0.490
10	0.530	10	0.494
15	0.577	15	0.493
20	0.605	20	0.490
25	0.655	25	0.485

This table shows:—

1. That accurate results can be obtained with H_2O_2 if *very* small excesses are used. We have never denied this.
2. That with increasing excesses of H_2O_2 the results are increasingly inaccurate. We contend that this is an undesirable feature in *any* reagent.
3. That accurate results are obtained by using ferrous sulphate in either small or large excess. This feature makes it superior to peroxide for *all* classes of steels, pig-irons, alloys, or any other ferriferous compound dealt with in steel works.

We trust the above statement will dispel Mr. Ramage's notion that during this discussion we have had in mind the assay of special steels only; we have desired only to emphasise the increased superiority of ferrous sulphate when dealing with such steels. Mr. Ramage's references to special steels are unfortunate. In his last letter he says:—"Hydrogen peroxide indicates the presence of the important rare metals in the special steels . . . and special methods of analysis may be applied to them." It is not possible to detect molybdenum during the titration, nor is it possible to make an accurate estimation of Mn in a steel containing a few per cents Mo if hydrogen peroxide is used.

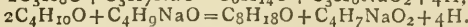
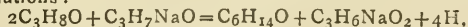
The question we raised respecting manganese alloys is certainly not answered by the paper in the *Transactions of the Chemical Society*, nor could it be because it depends entirely on facts which were not then publicly known. We have repeatedly titrated hydrogen peroxide against the permanganate in solutions containing 0.25 gm. of spiegel (after the Mn has been determined), and the amount of $KMnO_4$ required is always less than is required when the titration is made in acidified distilled water. If this difference is due, as we believe it is, to the reaction between ferric nitrate and hydrogen peroxide, surely Mr. Ramage ought to explain why, in the assay of alloys, he ignores the source of error he is so careful to avoid in steels.—We are, &c.,

FRED. IBBOTSON.

HARRY BREARLEY.

Bower Road, Sheffield.

Adion of Propylic and Normal Butylic Alcohols on their Respective Sodium Derivatives; Synthesis of Dipropylic and Dibutylic Alcohols.—Marcel Guerbet. —Propylic and normal butylic alcohols, when heated between 220° and 230° with their respective sodium derivatives, form condensed alcohols according to the equations:—



Further experiments prove this adion to be general, at least for alcohols of the form $R-CH_2-CH_2OH$.—*Comptes Rendus*, cxxixiii., No. 26.

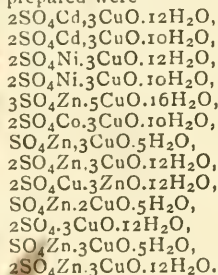
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiv., No. 1, January 6, 1902.

Preparation and Properties of Potassium Hydride.—Henri Moissan.—When potassium is kept for some hours in an atmosphere of hydrogen at a temperature of 350°, a transparent and crystalline layer of a hydrate is formed on the surface of the metal. This hydrate can be separated from the excess of metal by treatment with liquefied ammonia gas, in which case the metal is removed as potassium-ammonium. Analysis proves this hydride to have the formula KH. It is white and well crystalline, and instantly decomposed by water. It takes fire in cold fluorine, chlorine, and dry oxygen, and possesses very energetic reducing properties. It is comparable, both in appearance and chemical properties, to calcium hydride, which latter substance has been already described by the author.

Action of Cupric Hydrate on Aqueous Solutions of Metallic Salts.—A. Mailhe.—In a preceding paper, the author described the action of cupric hydrates on aqueous solutions of metallic chlorides and bromides. From this he was led to discover certain mixed basic salts analogous to those which he previously obtained by the action of oxides of mercury on aqueous solutions of salts of the same metals. He now describes the results obtained by the action of cupric hydrates on solutions of sulphates. The particular action examined is that of tetra-cupric hydrate, the only one which gives well crystalline and well defined compounds. Péligot's blue hydrate always leads to an uninteresting amorphous basic salt. The special salts prepared were—



Condensation of Acetylenic Carbides with the Ether Salts. Syntheses of Acetylenic Acetones and β -Ketonic Ethers.—Ch. Moureu and R. Delange.—The authors show that formic ethers attack sodium acetylenic carbides energetically, and that the action of water on the product of the reaction engenders the acetylenic aldehydes, $\text{R}-\text{C}\equiv\text{C}-\text{CHO}$. This reaction is, however, a complex one, and in nearly all cases the β -ketonic ethers corresponding to the ether salts employed are produced. Experiments were performed, using very varying proportions of two acetylenic carbides, cyanthyridene ($\text{C}_5\text{H}_{11}-\text{C}\equiv\text{CH}$) and phenylacetylene ($\text{C}_6\text{H}_5-\text{C}\equiv\text{CH}$), and on ten ether salts. The authors also devise a theory by which the reaction may be explained.

MISCELLANEOUS.

Direct Determination of the Avidity of Ammonia and of the Amines.—D. Kononov.—The method used is based on the measurement of the tension of the free bases in solution. The conditions are most favourable when one of the bases under comparison is not volatile at the temperature of the experiment (60°). The calculation is very simple in the case of weak solutions where the

presence of salts has only a negligible influence on the tension, which may be looked upon as proportional to the concentration. Under these conditions, exact values can be obtained of the reciprocal displacement of the amines by means of the formula $\text{H}'x + \text{H}''(1-x) = \text{H}$; where H' and H'' represent the tensions of the two amines in such cases where they are entirely in the free state in solution, and H the tension observed in a mixture of the salt of an amine with an equivalent amount of the other amine; x is the proportion displaced of one of the amines. The experiments were carried out with the chlorhydrates of ammonium, benzylamine, methylamine, dimethylamine, trimethylamine, and triethylamine. For the relative values of their avidity the figures correspond fairly well with their electric conductivity, but are not strictly proportional. With 0.5 normal concentrations the following values were found:—

Ammonia	1.00
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	0.97
CH_3NH_2	4.32
$(\text{CH}_3)_2\text{NH}$	3.90
$(\text{CH}_3)_3\text{N}$	2.21
$(\text{C}_2\text{H}_5)_3\text{N}$	1.68

These figures have no relation to the heats of neutralisation; thus, $(\text{CH}_3)_3\text{N}$ displaces 70 per cent of benzylamine from its salt, while the heats of neutralisation are 8.9 cal. for the first, and 12.9 cal. for the second.—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 193.

NOTES AND QUERIES.

Ammonium Chloride and Oxidising Agents.—I happened to heat together some ammonium chloride and sodium nitrate a short time ago, and found—rather to my surprise—that chlorine was given off in rather large quantities. I have since tried the effect of heating ammonium chloride with other oxidising agents, and find that chlorine is given off with potassium nitrate and potassium chlorate, but that ammonia is produced with manganese dioxide, mercuric oxide, and lead dioxide; the amounts of gases given off seem to vary with the temperature, thus causing an accurate quantitative estimation of the reaction to be difficult. I can find no mention of the reaction in any text-book, so should be much obliged if you could give me some information as to what happens in your "Notes and Queries," or refer me to a text-book in which I could find it.—F. W. HODGES.

MEETINGS FOR THE WEEK.

- MONDAY, 3rd.—Society of Arts, 8. (Cantor Lectures). "The Purification and Sterilisation of Water," by Samuel Rideal, D.Sc., F.I.C.
- Royal Institution, 5. General Monthly Meeting.
- TUESDAY, 4th.—Royal Institution, 3. "The Cell—its means of Offence and Defence—Immunity," by Allen Macfadyen, M.D., B.Sc.
- Society of Arts, 4.30. "The History of the Rosary in all Countries," by the Rev. Herbert Thurston, S.J.
- WEDNESDAY, 5th.—Society of Arts, 8. "Jamaica," by Herbert T. Thomas.
- THURSDAY, 6th.—Royal Institution, 3. "The Scot of the Eighteenth Century—I, At Home," by the Rev. John Watson, D.D. (Ian MacLaren).
- Society of Arts, 4.30. "The Coal Resources of India," by Wyndham R. Dunstan, F.R.S.
- Chemical, 8. "An Investigation into the Composition of Brittle Platinum," by W. N. Hartley. "Conversion of 1-Hydroxycamphene into β -Halogen Derivatives of Camphor," by M. O. Forster. "Tetrazoline" (Part II.), by S. Ruemann and H. E. Stapleton. "The Solubilities of the Calcium Salts of the Acids of the Acetic Acid Series" and "The Equilibrium between a Solid and its Saturated Solution at various Temperatures," by J. S. Lumsden. "The Influence of Temperature on Association in Benzene Solution, and the Value of the Molecular Rise of Boiling-point for Benzene at different Temperatures," by W. R. Innes. "The Magnetic Rotation of Ring Compounds—Camphor, Limonene, Carvene, Pinene, and some of their Derivatives," by W. H. Perkin, sen., F.R.S. "Polymerisation Products from Diazoacetic Ester," by O. Silberrad.
- FRIDAY, 7th.—Royal Institution, 9. "The New Mammal from Central Africa and other Giraffe-like Animals," by Prof. E. Ray Lankester, M.A., LL.D., F.R.S.
- SATURDAY, 8th.—Royal Institution, 3. "Landmarks in the History of Opera—IV., Wagner" (with Musical Illustrations), by W. H. Hadow, M.A., Mus. Bac.

THE CHEMICAL NEWS.

Vol. LXXXV., No. 2202.

RESEARCHES ON THE PRESSURE FORCES OF LIGHT.*

By PETER LEBEDEV.

(Concluded from p. 54).

THE following method was adopted for the measurements with the first calorimeter (Fig. 6). The mirror apparatus (Fig. 1) was drawn back so far on the sliding scale that the vane apparatus could be replaced by the calorimeter diaphragm, D. The calorimeter was then illuminated for five minutes, and from minute to minute the thermometer readings (and in the intervals the galvanometer readings also) were taken. Then the rays were stopped by a screen, and during the next five minutes, from minute to minute, the fall of the thermometer (and the zero point of the galvanometer) observed. A complete series of observations included five successive periods of illumination.

All observations were graphically represented, the readings of the thermometer being marked on squared paper and united by as even a curve as possible (Fig. 9).

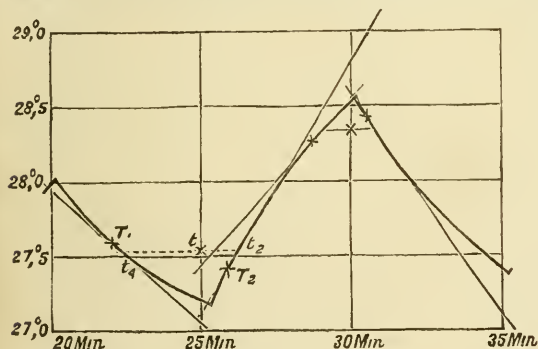


FIG. 9.

It is clear that after 10 secs. the movement of the mercury in the thermometer shows by a turning point when the light was turned on or off.

The great rapidity with which the calorimeter cools must be specially allowed for, for even in the interval of an observation neither the rate of warming nor of cooling is constant. For definite mean temperature of the surface of the calorimeter both rates have constant values, which, as is easily seen from the figure, are represented by tangents; for these constant values the points at which the tangents cut the ordinates give the temperature differences which would be reached in five minutes if both rates were constant, and the sum of both differences gives the total corrected rise of temperature.

But here an error in the estimation of true mean temperature may appear: the thermometer remains a little below this temperature in that it marks a lower temperature when the light is turned on, and a higher when the light is turned off. The fact that the thermometer marks a turning point after 10 secs. gives as a first approximation (and a sufficiently close one for us) the assumption that the thermometer is 20 secs. behind time. For a surface temperature, t , the points to be compared in the curve

would be not t_1 t_2 , but those dating 20 secs. back, i.e., T_1 and T_2 .

Such graphic determinations were made for two thermometers. Table III. gives a series of measurements.

TABLE III.

Calorimeter I. Water Equivalent 3.13 grms.

	Rate of warming.	Rate of cooling.	Total warming.	Galvano-meter deflection.	Reduced total warming. $G=100$.
				Divs.	$\frac{100}{G}$
I. {	1.67	0.63	2.30	140	1.64
	1.49	0.80	2.29	128	1.79
II. {	1.44	0.85	2.29	128	1.79
	1.31	1.10	2.40	122	1.97
III. {	1.38	1.08	2.46	129	1.91
	1.00	1.37	2.37	126	1.88
IV. {	1.30	1.15	2.45	123	1.99
	1.04	1.45	2.49	127	1.96
V. {	1.26	1.27	2.54	129	1.97
	0.93	1.50	2.43	126	1.93

Total warming in five minutes ($G=100$) 1.88 ± 0.09 .

The measurements were much simpler with the second calorimeter. The calorimeter was cooled with ethyl ether, then the light was turned on it, and the thermometer read from minute to minute (in the meanwhile the temperature of the bath and the galvanometer were observed). The results were represented graphically, and the point was marked at which the temperature of the calorimeter coincides with that of the bath (taking into consideration that the thermometer was 20 secs. behind time), and the tangents of the true rates of warming drawn at these points, and also the difference of the thermometer readings at intervals of 2.5 mins. Such a series of readings was taken three times; Table IV. gives the results of measurements.*

TABLE IV.

Calorimeter II. Water Equivalent 3.61 grms.

	Rise of temperature in five minutes.		Mean value.	Galvano-meter deflection.	Reduced rise of temperature. $G=100$.
	Tangents.	Differences.		Divs.	$\frac{100}{G}$
I.	2.40	2.41	2.40	159	1.51
II.	2.55	2.57	2.56	163	1.57
III.	2.43	2.50	2.46	158	1.56

Mean rise of temperature in five minutes ($G=100$) 1.55 ± 0.02 .

Hence, the quantity of energy per sec.—

$$E = \frac{1.55 \cdot 3.61 \cdot 4.18 \cdot 10^7}{300} = 7.74 \cdot 10^5 \text{ ergs.}$$

In our experiments the incident rays were not parallel but convergent; the small inclination of the incident rays would render a correction (of about 1 per cent) necessary; this correction balances the other errors in the measurements, and may be neglected. The calculation is sufficiently accurate if we employ the formula which holds good according to Maxwell and Bartoli for a beam of parallel rays.

For an absolutely black body the pressure based on the values of Table IV. is—

$$p = \frac{E \text{ (ergs)}}{3 \cdot 10^{10}} = 0.0000258 \text{ dynes.}$$

In order to express the results in such a way as to be readily compared at a glance, the value of Maxwell and Bartoli's pressure for an absolutely black body calculated from the calorimeter measurements was adopted as an arbitrary unit; this unit was called an M.B. unit.

* The results of Tables III. and IV. cannot be directly compared with one another since they refer to different adjustments of the thermo battery.

RESULTS.

	Apparatus I.				Apparatus II.				Apparatus III.			
	Calorimeter I.				Calorimeter II.				White.			
	White.	White.			White.	Red.	White.	Blue.	White.			
1. Thick platinum vane	1·8 ± 0·2	1·6 ± 0·1	1·5 ± 0·1	—	—	—	—	—	1·5 ± 0·1	1·4 ± 0·1	—	—
2. Thin platinum vane.	1·3 ± 0·2	—	—	—	—	—	—	—	1·2 ± 0·1	1·1 ± 0·1	—	—
Calculated	1·2	—	—	—	—	—	—	—	1·1	1·0	—	—
3. Platinum, thick ..	—	1·8 ± 0·1	—	—	—	—	—	—	—	—	—	—
4. Platinum, thin ..	—	2·0 ± 0·1	1·9 ± 0·2	1·8 ± 0·1	1·9 ± 0·1	(1·8 ± 0·8)	1·7 ± 0·1	(1·5 ± 0·5)	1·7 ± 0·1	2·0 ± 0·1	—	—
5. Aluminium, thick ..	—	—	2·3 ± 0·4	1·9 ± 0·1	—	—	—	—	—	—	—	—
6. Aluminium, thin ..	—	—	2·0 ± 0·1	2·3 ± 0·1	2·0 ± 0·2	(2·9 ± 0·8)	2·1 ± 0·1	(2·5 ± 0·5)	1·4 ± 0·2	1·7 ± 0·1	—	—
7. Nickel, thin	—	—	1·7 ± 0·3	1·2 ± 0·2	1·4 ± 0·1	(2·3 ± 0·5)	1·4 ± 0·2	(2·7 ± 0·9)	—	—	—	—
8. Mica	—	—	—	—	—	—	—	—	0·08 ± 0·05	0·13 ± 0·03	—	—

Expressed in these units, the result of Table I. is—

$$\rho = \frac{0\cdot0000308 \pm 0\cdot0000017}{0\cdot0000258} = (1\cdot19 \pm 0\cdot07) \text{ M.B.}$$

A direct measure of the reflecting power of the vane used was rendered useless owing to the inequalities of the thin metal leaf. Therefore, I observed with the photometer (Fig. 8) the reflecting power of the leaf of which the vanes were made. With this also the inequalities produced strong effects, and also a distinct colouration of the reflected light was apparent (especially in the case of nickel). The reflecting power observed for an angle of incidence of 25° is therefore given in Table V. without further reductions, and hence are calculated in M.B. units the pressure forces to be expected. For the sake of comparison the reflecting power according to Hagen and Rubens of a perfectly reflecting surface for normal incidence ($\lambda = 600 \mu\mu$) is given, and also the pressure forces calculated from this reflecting power. (The numbers for magnalium are given under aluminium).

TABLE V.

	Photometric measurements.		According to Hagen and Rubens.	
	ρ .	ρ .	ρ .	ρ .
		M.B.		M.B.
Platinum ..	0·5 ± 0·05	1·5	0·64	1·64
Aluminium ..	0·6 ± 0·05	1·6	0·83	1·83
Nickel	0·35 ± 0·05	1·4	0·65	1·65

I have omitted the calculations for mica because the observations were only made with one vane, and a control experiment with a thicker vane failed.

The results of the single series of experiments with the three kinds of vane apparatus are given in the accompanying table. When I proceeded to take measurements at lower temperatures, since the results at the temperature of the room were uncertain and fluctuating, I did not hope to attain in the experiments such a great degree of agreement with the calculations of Maxwell and Bartoli as is shown in the first experiments with Apparatus II. I believed at first that this agreement was accidental, and therefore replaced Calorimeter I. by Calorimeter II., and then Apparatus II. by Apparatus III.

The numerous observations which I made with Apparatus I. at the temperature of the room are decidedly less satisfactory than the later measurements, and are

therefore not given. Also, the measurements with vane 2 of Apparatus II. are omitted, because a supplementary microscopic examination showed insufficient platinisation. Unfortunately, with Apparatus III. only two series of measurements were taken because the arrangement was then destroyed by an accident.

The results are expressed in M.B. units; under each value is also given the mean variation of the position of the vane apparatus in the same units, all variations amounting to less than 0·15 M.B. being denoted by 0·1, and all under 0·25 by 0·2.

In estimating the accuracy of the final results the following considerations must be taken into account:—The variations of the deflection are given in the table; the magnitude of the pressure resulting from the deflection in absolute measure (direction force of the thread, distance of the scale, lever of the vanes, and corrections for the illuminated surfaces) may be determined with an accuracy of ± 8 per cent, the calculation of the absolute value of the M.B. unit from calorimeter measurements (water equivalent, rise of temperature of the calorimeter, and the ratio approximately equal to unity of the diaphragm to the vane) is accurate to ± 7 per cent; the error in the determination of the reflecting power may reach about 10 per cent. These errors in the measurements are exceeded by the inaccuracies in placing the vane in the centre of the real image of the diaphragm, and the possibility that the heat radiation of an illuminated vane is concentrated by the surface of the globe on other parts of the vane apparatus, and that the amount of heating alters at each oscillation of the vane apparatus. For white light the still admissible error of the measurement may be estimated at about ± 20 per cent.*

In experiments with blue and red light, where the available energy of radiation reaches scarcely one-fifth of that of white light, the disturbances caused by convection are the same, and therefore the errors correspondingly greater. The same holds good for the very small deflections (scarcely reaching 4 div. double deflection) in the case of mica. These control experiments are sufficient to confirm the fact that in these cases also no new effect of light showed itself, which would be comparable with the forces of Maxwell and Bartoli.

* A refinement of the methods of measurements would only essentially increase the certainty of the results if the arc lamp is replaced by another constant source of light.

I made, moreover, many comparative experiments with thick and thin platinum and aluminium vanes, but I did not succeed in establishing with certainty a perceptible radiometer difference; therefore within the limits of errors of observation the radiometer effect in the case of thin metal vanes is to be regarded as zero.

The results obtained may be collectively expressed as follows:—

1. An incident beam of light exercises a pressure both on an absorbing and a reflecting body. This force capable of doing work ("weight-moving") is dependent upon Crookes's already known secondary forces caused by heating, and upon the phenomena of convection.

2. These pressure forces of light are directly proportional to the quantity of energy falling on the body, and are independent of the colour of the light.

3. These pressure forces of light agree quantitatively within the limits of errors in the experiments with the "weight-moving" forces of radiation calculated by Maxwell and Bartoli.

Thus, the existence of Maxwell and Bartoli's pressure forces of light beams is experimentally proved.

ON PYRITE AND MARCASITE.*

By H. N. STOKES.

(Continued from p. 43).

III. DETAILS OF THE METHOD.

Necessary Precautions.

IN the following the precautions necessary to obtain strictly concordant results are given in detail, as well as a statement of the abbreviations which are permissible when only approximate results are desired.

To obtain accurate results it is necessary—

1. To employ sulphide absolutely free from oxidation products.
2. To avoid all access of free oxygen during the experiment.
3. To prevent the precipitation of basic ferric sulphate.
4. To prevent change of concentration due to loss by evaporation.
5. To make the titration with the greatest possible accuracy.

Preparation of the Material.

The mineral is somewhat finely ground, an operation which is greatly facilitated by adding water. After drying, it should be kept in a vacuum or in carbon dioxide until used. As both pyrite and marcasite oxidise rapidly when powdered, the oxidation products must be completely removed immediately before the experiment. About 1 grm. of the dry powder is washed by decantation two or three times with ether, two or three times with 20 per cent hydrochloric acid (1 part concentrated and 1 part water), and heated with the latter for a quarter of an hour or more, to remove basic salts, oxides of iron, and any contaminating sulphides or soluble silicates which may thus be extracted. It should be remarked that under these conditions pure pyrite evolves no perceptible hydrogen sulphide† if tested a few moments with lead-paper, while marcasite continues to give off minute amounts however long it may be heated with the acid. The evolution of hydrogen sulphide from pyrite indicates the presence of other sulphides. The material is then collected on a Gooch crucible fitted with a disk of Schleicher and Schüll hardened filter-paper, and washed with dilute hydrochloric acid, and then with water which has been

boiled and cooled in carbon dioxide. The washing is conducted in an atmosphere of carbon dioxide, and for this purpose I use the apparatus shown in Fig. 1, in which the wash-water is delivered from the dropping funnel, and the carbon dioxide, supplied from an ordinary automatic generator,* itself affords the pressure necessary to drive the liquid through the filter. The crucible is then sucked out by attaching a pump to the outlet tube, placed for a moment on a blotter to remove most of the water, and transferred to a vacuum desiccator containing sulphuric acid, and filled with carbon dioxide, which is then exhausted. The use of carbon dioxide in this connection is essential, as even the best vacuum attainable by ordinary means contains enough oxygen to produce sensible oxidation. The drying is complete in half-an-hour.

Oxidation Apparatus.

The decomposition apparatus is represented in Fig. 2. A flask holding about 400 c.m.³ is provided with a doubly perforated rubber stopper which has been well boiled out in caustic soda; through this pass the inlet tube for carbon dioxide and the condenser. The latter consists of an elongated calcium chloride tube, into which fits loosely a test-tube through which cold water passes. The condenser has a hole at *a* to allow the passage of the steam, so that the return water drops quietly from the end of the tube. It is absolutely essential to prevent the return water from striking the sides of the flask or inlet tube, as at such points a film of basic sulphate invariably forms.

The flask is placed up to the stopper in a cylinder of asbestos board provided with windows of mica or glass on opposite sides, to admit of watching the operation. This rests on a plate† of asbestos containing a circular hole covered with gauze, and is closed at the top by a similar plate. The object of this arrangement is to prevent as far as possible the condensation of water on the sides of the flask; when this occurs, a ring of basic sulphate tends to form at the surface of the liquid. About 250 c.m.³ of the standard solution are used. The small loss by wetting of the condenser is compensated by having it wet at the outlet.

Blank experiments of this apparatus lasting two hours show no deposition of basic salt, no loss by volatilisation (if the ingoing gas is saturated with moisture), and no reduction of the ferric salt.

Details of the Operation.

As the solution contains enough air seriously to affect the results, and as the percentage of sulphur oxidised varies with the temperature, it is necessary to introduce the substance into the boiling liquid, and not until all the air has been boiled out. For this purpose it is rapidly placed in the small bucket, shown on a large scale in Fig. 2, A, which consists of a small test-tube cut off and constricted at the bottom, and provided with a loosely fitting platinum disk, made tight by pouring in a little iron-free asbestos emulsion, such as is used in Gooch crucibles. The bucket is suspended by a platinum wire, and is dropped into the liquid after this has boiled ten minutes. It is necessary that the powder shall disseminate through the liquid, and not settle out on the bottom for any considerable time. If this be not the case, abnormal results are obtained, for reasons which are not clear. The powder, as well as the apparatus, must therefore be strictly free from grease, and, to aid the dissemination, the apparatus must be so mounted on a stand as to admit of agitating the liquid until the powder remains suspended. Pyrite disseminates readily, but marcasite shows a strong tendency to flocculate at first, and the two may generally be distinguished by this means.

During the whole operation a very slow current of carbon dioxide is passed through. This must, of course,

* From the *Bulletin of the U.S. Geological Survey*, No. 186.

† One-half grm. pure powdered pyrite, boiled in the decomposing apparatus for one hour with 7 per cent sulphuric acid, in a slow current of carbon dioxide, caused a slight blackening of lead paper placed in the top of the condenser.

* Liquefied carbon dioxide contains air, and should not be employed.

† In the figure the flask is represented as elevated above the plate. During the boiling it must rest on it.

be absolutely free from oxygen, and as some air is present even in the most carefully prepared carbon dioxide, I always pass it over red-hot copper.* It must also be free from hydrogen sulphide, which is not always the case, and it can easily be freed from this by passing it through a tube filled with beads, and containing saturated copper sulphate solution.

The greater part of the ferric sulphate is reduced after a few minutes' boiling, but in order to effect complete reduction the boiling should be continued two hours. The liquid is then cooled and filtered through dry filters into two accurate 100 c.m.³ flasks, which are filled with carbon dioxide, and placed in cylinders of the same. In order entirely to avoid contact with the air, it is driven over

This generally gives a faint reaction for ferric iron. If it is decidedly red, either the reduction is incomplete or the mineral contains notable amounts of copper. (For the explanation of this see "Experiment with Ferrous and Cuprous Sulphates," *prox.*).

As small errors in titration produce considerable deviation, an accurately calibrated burette should be used, so narrow that the bottom of the meniscus can be distinctly seen against a light. Those burettes which have the graduation carried half-way around the tube are particularly good for accurate reading. The permanganate should have a strength of about 1.5 grms. per litre, and should be run in only to the very faintest change of colour, as compared with a ferric alum solution of approximately the same strength and acidity.

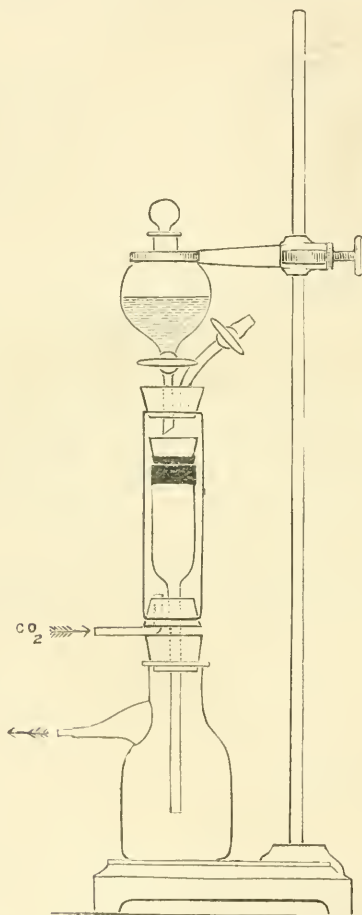


FIG. 1.—APPARATUS FOR WASHING SULPHIDES IN AN ATMOSPHERE OF CARBON DIOXIDE.

through the inlet tube by means of carbon dioxide introduced through the condenser. The flasks are then brought to the temperature of the permanganate to be used, and the contents are transferred to flasks containing sulphuric acid, and filled with carbon dioxide, and titrated. After reducing by hydrogen sulphide, filtering off the sulphur, and expelling the hydrogen sulphide by boiling in a carbon dioxide current, the total iron is titrated. A portion of the remaining solution should always be tested with sulphocyanate to ascertain the extent of the reduction.

* When many determinations are to be made, it is convenient to place the copper in an iron gas-pipe, water jacketed at both ends if necessary.

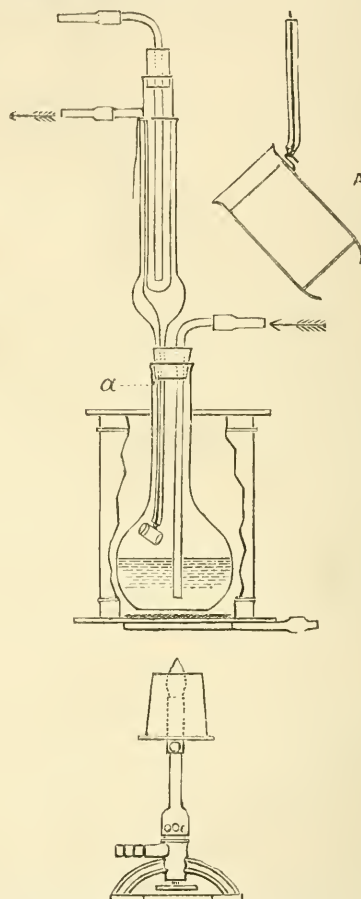


FIG. 2.—APPARATUS FOR OXIDISING SULPHIDES WITH FERRIC SOLUTION.

When less accurate results are required the mineral, after extraction with acid, may be simply collected on a hardened filter, washed with acid and water, and dried in the vacuum; special purification of the carbon dioxide, filtering in a carbon dioxide atmosphere, and other exceptional precautions may be omitted. Results made in duplicate in this way may differ 3 or 4 per cent.

Accuracy of the Method.

If 100 c.m.³ solution and a permanganate of 1.5 grms. per litre be used in titrating an excess of 0.1 c.m.³ permanganate, or an oxidation of 0.003 grm. of the material, gives the following errors in the value of p :—

	a.	b.	c.	Oxidation of 0.0003 grm. sulphide.
Pyrite ..	+1.00	+0.12	-1.00	-1.00
Marcasite	+0.20	+0.05	-0.20	-0.15

Special care is therefore necessary in standardising the original solution and in the final titration. Practically, duplicate determinations with pyrite tend to agree more closely than those with marcasite, as seen in the table below. This is perhaps due to the greater tendency of marcasite to flocculate, as indicated above, and to its greater tendency to oxidise, although the influence of the latter is less than in the case of pyrite. The influence of various impurities is considered later on.

(To be continued),

EXPERIMENTS RELATIVE TO THE CONSTITUTION OF PECTOLITE, PYROPHYLLITE, CALAMINE, AND ANALCITE.*

By F. W. CLARKE and GEORGE STEIGER.

(Continued from p. 55).

Analcite.

ANALCITE, from many points of view, is a species of peculiar interest, and of late years it has received a great deal of attention. Its formula may be written in various ways, especially as regards the interpretation of its one molecule of water; but evidence too often has yielded before preconceived opinion. Additional evidence is now available, partly from the experiments of Friedel and partly from the data obtained during the present investigation.

The analcite examined by us was in well developed crystals from Wasson's Bluff in Nova Scotia. A uniform sample was prepared as usual, and the analysis given below is contrasted with the theoretical composition required by the accepted empirical formula $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$.

Analysis.

	Found.	Calculated.
SiO_2	57.06	54.55
Al_2O_3	21.48	23.18
Fe_2O_3	0.13	—
CaO	0.16	—
Na_2O	12.20	14.09
H_2O at 100°	0.58	—
H_2O over 100°	8.38	8.18
	99.99	100.00

Fractional Water.

At 100°	0.58
At 180°	1.16
At 260°	3.64
At 300°	1.57
Low redness	1.90
Full redness	0.11
Blast	none
	8.96

The fractional water determinations were made by heating in an air-bath to constant weight at each temperature up to 300° , and finally over the direct flame. The first fraction, at 100° , is evidently hygroscopic or extraneous water, which can be disregarded. The remainder of the water, 8.38 per cent, belongs to the species. The significance of the analytical figures will be considered later.

Upon boiling the powdered analcite with sodium carbonate solution—250 grms. to the litre, as in all the preceding experiments—0.73 per cent of silica was extracted. After ignition, the mineral in two determinations yielded

1.46 and 1.38 per cent respectively. The splitting off of silica is therefore very slight; and one of the formulæ proposed by Doelter (*Neues Jahrb. für Min.*, 1890, vol. i., p. 133), $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 + 2\text{H}_2\text{SiO}_3$, may be set aside as improbable. Metasilicic acid or an acid metasilicate can hardly be present in analcite, although the possibility of a neutral metasilicate, as indicated by the empirical formula, is not excluded. By Doelter's formula one-half of the silica ought to be removable.

Upon heating analcite with dry ammonium chloride, results of a remarkable character were obtained. Sodium chloride was formed which could be leached out by water and measured, while ammonia free from chlorine was retained by the residue to a notable and surprisingly stable degree. The experiments in detail were as follows:—

- Analcite, mixed with four times its weight of ammonium chloride was heated for four hours to 350° . There was a gain in weight of 2.18 per cent, and 6.10 per cent of soda, or one-half of the total amount, was converted into NaCl, which was leached out by water, examined as to its purity, and weighed. In the residue 1.20 per cent of silica was extractable by sodium carbonate, showing that no more splitting off had occurred than was previously observed. The gain in weight, as will be seen from subsequent experiments, is due to the fact that all of the NH_4Cl had not been driven off; or else that more water was retained.
- Analcite was ground up with four times its weight of NH_4Cl , heated for several hours, re-ground with another fourfold portion of chloride, and heated to 350° for twenty-one hours. Gain in weight, 0.08 per cent; 5.57 per cent of soda was extracted as chloride.
- Analcite heated to 350° for eight hours, with four times its weight of NH_4Cl . Loss of weight, 0.10 per cent.
- Six grms. of mineral and 28 of chloride, mixed by thorough grinding, were heated to 350° for fourteen hours; then were re-ground with 28 grms. of fresh NH_4Cl and heated for thirty-five hours. Loss of weight, 0.13 per cent; 5.07 per cent of soda was extracted as chloride, plus 0.14 of ammonium chloride unexpelled; 2.03 per cent of silica was rendered soluble in sodium carbonate.

So far, three facts are noticeable. First, the weight of the mineral after treatment is almost exactly the same as before; showing that gains and losses have balanced each other. Second, little silica has been split off. Third, approximately—but not rigorously—one-half of the soda had been converted into NaCl. In A, it was exactly half; in the other experiments, a little less than half. Furthermore, in the sodium chloride dissolved out there is only a very little ammonium chloride, amounting at most to 0.14 per cent, calculated upon the weight of the original mineral.

In the residue of the analcite after extraction of sodium chloride, abundant ammonia can be detected, with either no chlorine or at most a doubtful trace. If, however, the unleached mineral, still retaining its sodium chloride, be heated strongly, say from 400° up to redness, NH_4Cl is re-generated and given off. Its absence, as such, both from the leach and the residue was repeatedly proved. The ammonia and water retained by the analcite after heating to 350° with ammonium chloride were several times determined, and the following percentages, still reckoned on the original mineral, were found:—

	NH_3 .	H_2O .
In B	2.03	2.25
In C	2.19	2.00
In D	2.36	1.89
In D	2.35	—
In D	2.06	—
Mean	2.20	2.04

Correcting the ammonia for the 0.14 of NH_4Cl found in D, the mean value becomes 2.15. This permanent ammonia is not given off upon warming the material with caustic soda solution, and is therefore not present as a salt. The determinations of it were made by three distinct methods, and there is no possible doubt as to its presence and character.

The composition of the analcite after the treatment with ammonium chloride may now be considered, with the subjoined combination of the data. The NaCl in A, 11.50 per cent, was in material which had gained 2.18 per cent, and is subject to a correction which reduces the figure to 11.26. In B, C, and D the corresponding correction is so small that it may be neglected. The last column gives the composition of the leached residue, re-calculated to 100 per cent, after deduction of NaCl and the soluble silica. The letters refer back to the several experiments, and the little iron is included with the alumina.

	A.	B.	C.	D.	Average.	Residue.
Soluble SiO_2 ..	1.20	—	—	2.03	1.61	—
Insoluble SiO_2 ..	—	—	—	54.96	54.96	62.59
Al_2O_3	—	—	—	21.37	21.37	24.34
CaO	—	—	—	0.16	0.16	0.18
NaCl	11.26	10.50	—	9.57	10.44	—
Na_2O	—	—	—	7.12	7.12	8.11
NH_3	—	2.03	2.19	2.21	2.15	2.46
H_2O	—	2.25	2.00	1.89	2.04	2.32
				99.31	99.85	100.00

The analcite residue, like the original mineral, is completely decomposable by aqueous hydrochloric acid. It may be a mixture, but it seems more probable that it is a definite compound, for it approximates in composition to the formula $\text{H}_2\text{Na}_2\text{Al}_4\text{Si}_8\text{O}_{24}\cdot\text{NH}_3$.

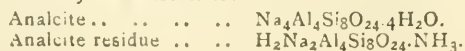
This represents a quadrupled analcite formula, in which half of the sodium is replaced by hydrogen, and with NH_3 in place of $4\text{H}_2\text{O}$. The analytical comparison is as follows:—

	Found.	Calculated.
SiO_2	62.59	61.46
Al_2O_3	24.34	26.12
CaO	0.18	—
Na_2O	8.11	7.94
H_2O	2.32	2.30
NH_3	2.46	2.18
	100.00	100.00

The agreement is not close, but it is close enough to be suggestive and to indicate the character of the reaction which has taken place. It needs, however, verification by additional experiments upon other preparations, and upon analcite from other sources. In this connection it may be well to reiterate that the substance was prepared by very long heating at 350° , and is therefore stable at that temperature.

An interesting feature of these experiments is their harmony with the researches of G. Friedel (*Bull. Soc. Min.*, 1896, vol. xix., p. 94), who has shown that the water of zeolites may be replaced by ammonia and other substances, without change of the crystalline structure. In the case of analcite, ammonia was taken up to the extent of 2.04 per cent, or almost exactly the amount found in our analcite residue. The great difference between Friedel's method of experimentation and ours renders the agreement all the more striking, and sustains our belief that the mineral and the residue are compounds of the same general order. We hope to continue our experiments and to extend our investigations to other zeolites.

If, now, analcite and its derivative, our analcite residue, are analogous compounds, the relation between them is expressed by these formulæ:—



That is, the minimum molecular weight assignable to analcite is represented by four times its empirical formula. Other interpretations of the evidence are possible, but this appears to be the simplest. The water of analcite, as Friedel has shown, must be regarded as water only, not as hydroxyl, for it can be expelled by heat without destruction of the crystalline nucleus, the anhydrous salt, and is taken up again from moist air. But whatever its mode of union may be, the amount of water corresponds to the simple molecular ratio which is indicated in the formula of the species. One molecule of analcite holds a certain definite number of water molecules, and Friedel's observations are not incompatible with the idea that these are retained with varying degrees of tenacity. This idea is suggested by the various series of fractionation experiments which have been made from time to time by independent workers, even though the data are not by any means concordant. Thus, Lepierre (*Bull. Soc. Chim. de Paris*, 1896, Series 3, vol. xv., p. 561) found that half the water of analcite was driven off at or below 300° , the other half above 440° . In our own experiments three-fourths was expelled at 300° , the remaining fourth being held up to a much higher but undetermined temperature. In both series the water fractions are representable by fourths, but Friedel's experiments (*Bull. Soc. Min.*, 1896, vol. xix., p. 363) indicate a continuity of loss in weight of quite a dissimilar order. Friedel holds that all of the water fractionations heretofore made upon analcite are fallacious, and that no definite fractions can be identified, a conclusion strongly supported by his own data, even though the proof is not absolutely positive. The most that can be said is that the weight of evidence so far is in favour of Friedel's contention, but that additional investigation is necessary in order to reconcile all discrepancies. The full significance of the water in analcite remains unknown.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1902.

Prof. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

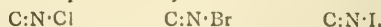
(Concluded from p. 56).

*2. "The Constitution of Hydrocyanic, Cyanic, and Cyanuric Acids." By F. D. CHATTAWAY and J. M. WADMORE.

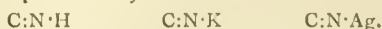
A study of the behaviour of cyanogen chloride, bromide, and iodide shows that they possess the typical and characteristic properties of compounds in which halogen is attached to nitrogen.

They react, for example, quantitatively with solutions of hydriodic acid, sulphurous acid, and hydrogen sulphide, hydrocyanic acid being in each case reformed, whilst iodine, sulphuric acid, and sulphur respectively are produced.

They must, consequently, be regarded as imino-derivatives, and be represented by the constitutional formulæ,—



The ease with which the cyanogen halogen compounds can be formed from hydrocyanic acid and its salts, and again transformed into them, makes it in the highest degree probable that these also have the imino-constitution, and must be represented by formulæ such as—



Since the cyanides and cyanogen halogen compounds have the above structure, their relations with cyanic acid

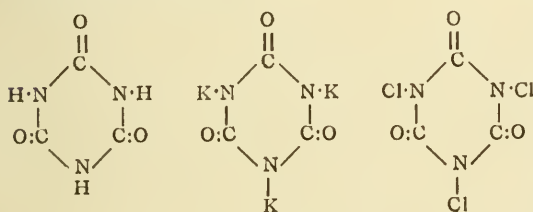
and the cyanates point to the probability of the latter also having the *iso*-constitution:—



Cyanuric acid also yields a derivative in which all its hydrogen is replaced by chlorine, and which has the composition $\text{C}_3\text{O}_3\text{N}_3\text{Cl}_3$. It is formed by the action of chlorine on a solution of potassium cyanurate. It is a white powder, insoluble or soluble only with decomposition in most ordinary solvents, which under the microscope is seen to consist of short prisms, *m. p.* 245° .

Its behaviour shows that the whole of its chlorine is attached to nitrogen. It liberates chlorine when treated with hydrochloric acid, iodine with hydriodic acid, and oxidises sulphurous to sulphuric acid; it reacts explosively with a strong solution of ammonia, nitrogen being evolved, and also with a solution of hydrogen sulphide, setting free sulphur; cyanuric acid is in each case reformed.

Since cyanurates are readily and completely converted into this trichlorimino-derivative, and the latter in many reactions equally readily and completely again into cyanuric acid, the conclusion is justified that the latter and its derivatives are imino- and not hydroxy-compounds, and assuming the ring structure, they must therefore be represented by the formulæ:—



A similar study of the behaviour of cyanuric chloride and bromide shows that in them the halogen is attached to carbon and not to nitrogen.

DISCUSSION.

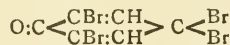
Professor DOBBIE said that in a paper (Hartley, Dobbie, and Lauder, *Trans.*, 1901, lxxix., 848) on the absorption spectra of cyanogen compounds, it had been pointed out that if cyanuric acid possessed the formula usually assigned to it, it differed from all substances hitherto examined in which carbon and nitrogen atoms were united by alternate double and single bonds in showing no selective absorption. This was the case, however, not only with the derivatives of cyanuric, but also of those of *isocyanuric* acid, so that if cyanuric acid possessed the imino-structure attributed to it by the authors, there still remained the difficulty of satisfactorily representing the constitution of the *iso*-derivatives. All that spectroscopic examination proves is that it is extremely unlikely that any of these compounds possess a structure analogous to that of pyridine or dimethylpyrazine.

Mr. C. E. GROVES said that the very interesting substance, $\text{C}_3\text{O}_3\text{N}_3\text{Cl}_3$, to which the authors had given the name of trichloraminocyanuric acid, seemed to have rather the properties of a hypochlorite. Several ring compounds were known somewhat analogous to it in properties, of which the constitutions were accurately known in so far that the chlorine was certainly not attached to nitrogen; such, for instance, was the compound obtained by chlorinating trichloro-*orcinol*, $\text{C}_6\text{Cl}_3\text{Me}(\text{OH})_2$, which might be represented by the hypochlorite formula, $\text{C}_6\text{Cl}_3\text{Me}(\text{OCl})_2$. If this view were adopted, the formula of the new substance might be represented as $\text{C}_3\text{N}_3(\text{OCl})_3$, in harmony with that usually assigned to cyanuric acid, $\text{C}_3\text{N}_3(\text{OH})_3$.

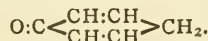
Dr. LAPWORTH thought that, even if the halogen derivatives referred to had the constitutions which it was proposed to assign to them, it did not follow that the acids from which they are obtained had the same structure. The conclusions drawn were no doubt correct,

but this had been decided by physical methods. Reasoning based on the assumption that a substituting atom or group takes up the position originally occupied by the atom displaced could only be accepted with the utmost caution when the molecule is of a labile type.

Thus, in the replacement of the metal in ethyl sodioacetate by alkyls, the new group becomes attached to the carbon atom, but it is not generally conceded that the metal in the original compound occupied that position. Again, by the action of bromine water on phenol, a tetrabromo-substitution product having the structure—

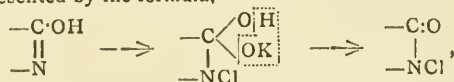


is obtained (*Ber.*, 1900, xxxiii., 674), but this is not a sufficient reason for representing phenol by the formula—



In such cases the reactions are open to several interpretations, and in the present case the substitution experiments may be explained equally well by using the alternative formulæ for the acids.

Dr. FORSTER pointed out that the conversion of cyanuric acid into the chloro-derivative by the action of chlorine on a solution of the acid in potassium hydroxide is an argument which supports the hydroxylic representation of cyanuric acid quite as strongly as the iminic, the change represented by the formula,—



leading easily from hydroxylic cyanuric acid to the nitrogen chloride derivative.

Dr. TRAVERS remarked that though the authors had referred to the work of Hartley and others as supporting their theory, the researches of these same investigators on isatin and its methyl derivatives pointed to the danger of accepting such conclusions. Since *ketonic* isatin gives rise, by treating its salts with methyl iodide, to *enolic* methyl isatin, obviously no conclusion could be drawn from such a reaction, which they explain on the basis of the ionic theory.

Professor DUNSTAN was of opinion that in general the tautomerism of these cyanogen derivatives renders it impossible to assign to any one of them a formula which will satisfactorily account for all its reactions. The authors had obtained a very interesting chlorine derivative of cyanuric acid, but its behaviour did not appear to be inconsistent with its being regarded as containing chlorine in the place of the hydrogen of three hydroxyl groups. He considered improbable the authors' explanation of its decomposition by hydrochloric acid giving free chlorine.

Dr. CHATTAWAY, in reply, said that their work neither proved nor disproved the cyclic constitution of cyanuric acid; it only showed that, whatever the formula, the whole of the hydrogen was attached to nitrogen, and therefore the hydroxylic formula was not possible.

The stability of the chlorine derivative of cyanuric acid, and the analogy of its reactions with those of substances such as nitrogen iodide and cyanogen iodide, showed that it could not contain —O—Cl groups.

*3 "A Modification of Zeisel's Method for the Estimation of Methoxyl Groups." By J. T. HEWITT and T. S. MOORE.

The authors described a modification of Zeisel's well-known method in which the condenser supplied with water at 40° is replaced by a fractionating column; this is so efficient that the potash bulbs containing water with red phosphorus in suspension may be dispensed with. The time taken in fitting up the apparatus and in carrying out the operation is much less than in Zeisel's original method. Experimental data were given showing the accuracy attainable.

*4. "A New Colour Reaction of Hydroxylamine." By W. C. BALL, B.A.

During the course of some experiments on the action of hydroxylamine salts on nickel sulphide, the author obtained an intense purple colouration, which proved eventually to be independent of the presence of nickel or any other metal.

The production of this colour is a very delicate test for hydroxylamine, as solutions so dilute as no longer to reduce Fehling's solution perceptibly, either in the cold or on boiling, easily respond to this test. The best method of applying the reaction is to boil the hydroxylamine solution with one or two drops of yellow ammonium sulphide solution until a precipitate of sulphur is produced; two or three cubic centimetres of 0.880 ammonia solution are then added, and finally an equal volume of strong pure alcohol.

The purple colour thus developed exhibits a characteristic absorption spectrum, consisting of a wide band covering the yellow, orange, and part of the green. In stronger solutions, the violet and blue are absorbed, and in very strong solutions the green rays also, so that the only light transmitted is a band in the red.

With a dilution of 1 part of hydroxylamine in 2000 of water the colouration is intense, and the band very distinct; with a dilution of 1 part in 300,000 of water, the colouration is still strong, and the band perceptible in 3 centimetres thickness of the solution. By means of this test hydroxylamine may be detected when the dilution does not exceed 1 part in 500,000 of water.

The production of the colour is well adapted for showing the formation of hydroxylamine by the action of metals, for example, tin, on nitric acid. It also serves as a very good means of distinguishing hydroxylamine from hydrazine, as the latter base does not produce the colour. The coloured substance is also produced, and can be obtained in the solid form, by the action of dry ammonia on an alcoholic solution of sulphur monobromide, or an acetone solution of nitrogen sulphide in presence of a little hydrogen sulphide.

The colouring matter seems to be the same as that observed by Fordos and Gélis when nitrogen sulphide containing sulphur is treated with alcoholic potash.

The absorption spectrum of the compound appears to be identical with that of Moissan's sulphammonium, obtained by the action of liquid ammonia on sulphur.

The author is endeavouring to obtain the substance pure enough for analysis.

*5. "On the Sensitiveness of a Thermoregulator." By A. W. C. MENZIES.

The following details have been recorded, as it is not generally known within what small limits of temperature a bath may be kept constant, using gas heating and the ordinary form of regulator. The glass "horse-shoe" reservoir was of the usual form, with a capacity of 390 c.c. and an outer surface of about 650 sq. c.m.; to this reservoir the ordinary U-form regulating tube which contains mercury, was fused on, and the glass connections so bent that all the tubes containing enclosed liquid were under the water of the bath. As toluene was used for the expanding liquid, the stop-cock that closes one limb of the U-tube was lubricated with syrupy phosphoric acid. The bath held 14 litres and was of enamelled iron, with no jacket. The stirrer was driven by a small electromotor, and care was taken that a portion of the vibration of the motor was communicated to the regulator, thus aiding the free movement of the mercury in response to the pressure of the toluene. The gas supply to the by-pass was adjusted by a screw-clip in such a way that the by-pass flame alone was nearly sufficient to maintain the temperature. Using a tube of 3.1 m.m. bore for the outer limb of the regulator, the temperature of the bath can be kept constant at 18° within a total range of 0.008°, that is, 0.004° on each side of the middle point. After twenty-four days, using unfiltered coal-gas, the actual temperature was the same as at starting, and the

closeness of regulation was found still within the above limits. If narrower tubes be used, it is well to dry and filter the gas. The inlet tube that leads the gas down to the surface of the mercury is cut off square, and should be so wide that on trial the mercury rises higher in it than in the space between it and the regulator tube. A bore of 1.9 m.m. for the outer limb of the regulator gave a temperature variation in the bath of not more (though probably less) than 0.0025 (total range). The difference of temperature between bath and room was 6—7°; if the flame were removed, the bath was found to cool 0.1° in 4.5 minutes. With this regulator, a well-tapped calorimetric thermometer by Golaz, divided into fiftieths of a degree, remained apparently stationary to an estimated tenth-division, as also did a "Beckmann" thermometer graduated directly to hundredths. The limits actually registered by two large special alcohol thermometers (one with a bulb of extremely thin glass 180 m.m. long and 5 m.m. in diameter) were less than those stated above, which are given after making due allowance for the sluggishness of action of such thermometers.

6. "Myricetin." Part II. By A. G. PERKIN.

Myricetin (*Trans.*, 1896, 1287), air-dried, has the formula $C_{15}H_{10}O_8 \cdot H_2O$, is anhydrous at 160°, and melts about 357°. The compound previously obtained by the action of bromine is *tetrabrom-myricetin*, $C_{15}H_6Br_4O_8$, and is converted by hydriodic acid into myricetin. *Myricetin-pentamethyl ether*, $C_{15}H_5O_3(OCH_3)_5$, m. p. 138—139°, forms a *monoacetyl* derivative, $C_{15}H_4O_3(OCH_3)_4(C_2H_3O)$, colourless needles, m. p. 167—170°, and on decomposition gives gallic acid trimethyl ether and phloroglucinol monomethyl ether, the latter identified by its diazobenzene derivative (m. p. 250—252°). *Myricetinhexaethyl ether*, $C_{15}H_4O_2(OEt)_6$, almost colourless needles, m. p. 149—151°, yields gallic acid triethyl ether and a phenol, probably phloroglucinol diethyl ether (azobenzene compound, yellow needles, m. p. 163—165°). Acetylmyricetin melts at 211—212° and not at 204—206° as previously stated.

Myricetin, air-dried, $C_{21}H_{22}O_{13} \cdot H_2O$; at 160°, $C_{21}H_{22}O_{13}$, pale yellow leaflets, m. p. 199—200°; a new glucoside, occurs in the bark of the *Myrica nagi*, and is decomposed by acid into myricetin and rhamnose, $C_{21}H_{22}O_{13} + H_2O = C_{15}H_{10}O_8 + C_6H_{14}O_6$. It closely resembles quercitrin.

7. "The Colouring matters of Green Ebony." By A. G. PERKIN and S. H. C. BRIGGS.

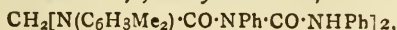
Green ebony is a yellow dyewood, probably *Excoecaria glandulosa* or *Jacaranda ovalifolia*, until recently employed in this country. It contains two crystalline colouring matters, *excoecarin* and *jacarandin*, in minute quantity. *Excoecarin*, $C_{13}H_{12}O_5$, yellow needles, m. p. 219—221°, a weak, substantive dyestuff with animal fibres, forms a *tribenzoyl* compound, $C_{13}H_9O_5(C_7H_5O)_3$, colourless needles, m. p. 168—171°, and a *dimethyl ether*, m. p. 117—119°, yellow needles, giving fluorescent solutions. On fusion with alkali, it yields *hydrotoluquinone* ($CH_3:O:O=1:2:5$), and *hydroquinone carboxylic acid*, the latter apparently derived from the former. Bromine in presence of alcoholic potassium acetate forms *excoecarone*, $C_{13}H_{10}O_5$, copper coloured needles, m. p. about 250°, which on reduction is re-converted into *excoecarin*. Alcoholic quinone solution gives a similar compound ($C_{15}H_{14}O_7$?), green leaflets, m. p. 190°, which is possibly a quinhydrone derivative. *Jacarandin*, $C_{14}H_{12}O_5$, yellow plates, m. p. 243—245°, resembles luteolin in dyeing property, and gives a *diacetyl*, $C_{14}H_{10}O_5(C_2H_3O)_2$, yellow needles, m. p. 192—194°, and a *dibenzoyl* derivative, $C_{14}H_{10}O_5(C_7H_5O)_2$, yellow prismatic needles, m. p. 167—169°. With alcoholic potassium acetate, the *salt*, $C_{28}H_{23}O_{10}K$, yellow needles, results, and on fusion with alkali, an acid, apparently derived from catechol, is formed. The wood contains also two orange-coloured resins, one of which is a yellow dyestuff, but the other is devoid of tinctorial property.

8. "The Action of Methylene Iodide on Aryl- and Naphthyl-amines: Diarylmethylenediamines, Acridines, and Naphthacridines." By A. SENIER and W. GOODWIN.

The compounds obtained by the interaction of methylene iodide and arylamines (*Trans.*, 1901, lxxii., 254) were believed to be arylmethylenediamines. The study of these compounds now proves that in the case of the reaction with aniline, the toluidines, and xylidine, such diamines are formed. With ψ -cumidine, however, the well-defined, beautiful, yellow, crystalline compound which results is shown to be a condensation product. Its analysis, vapour density, the fluorescence of its solutions, and the analogy of its formation to the anthracene synthesis of Friedel and Crafts (*Ann. Phys.*, 1887, [vi.], xi., 263), and the acridine synthesis of Bernthsen and Bender (*Ber.*, 1883, xvi., 1802), indicate it to be an acridine:—hexamethylacridine. This view is confirmed by the exactly parallel behaviour of both α - and β -naphthylamine with methylene iodide, giving rise to similar compounds, and the identity of the β -compound with the β -naphthacridine already known. This naphthacridine was discovered by Reed, using a different reaction (*Fourm. Prak. Chem.*, 1886, [ii.], xxxiv., 160; 1887, xxxv., 298), and has led to interesting results in the hands of Morgan (*Trans.*, 1898, lxxiii., 536).

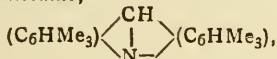
The further study of the properties and constitution of hexamethylacridine and α -naphthacridine is being proceeded with, and is reserved for a future communication.

The following compounds were described:—*Diphenylmethylenediamine*, $\text{CH}_2(\text{NHPh})_2$, dark yellow powder, m. p. 65–67°. *Diphenylmethylenediamine platinichloride*, $(\text{C}_6\text{H}_5)_2\text{N}_2\text{H}_2\text{PtCl}_6$, olive-green powder. *Dicarbanilido-diphenylmethylenediamine*, $\text{CH}_2(\text{NPh}\cdot\text{CO}\cdot\text{NHPh})_2$. *Di-tolylmethylenediamines*, $\text{CH}_2(\text{NHC}_6\text{H}_4\text{Me})_2$; *o-derivative*, colourless crystals, m. p. 156–157°; *p-derivative*, pale yellow crystals, m. p. 149–150°; *m-derivative*, yellow, amorphous but not definite. *Dixylylmethylenediamine*, $\text{CH}_2(\text{NHC}_6\text{H}_3\text{Me}_2)_2$, pale yellow, large foliate crystals, m. p. 127–128°. *Dixylylmethylenediamine platinichloride*, $(\text{C}_7\text{H}_{22}\text{N}_2)\text{H}_2\text{PtCl}_6$, golden-yellow powder. *Dicarbanilidocarbanilidodixylylmethylenediamine*,—

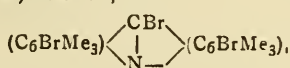


yellowish-white substance resembling wax, yielding colourless needles when re-crystallised, m. p. 203°.

Hexamethylacridine,—

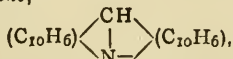


fine yellow needles, m. p. 221–222°, sublimes readily, solutions fluorescent. *Hexamethylacridine, picrate*, $(\text{C}_{19}\text{H}_{21}\text{N})\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, fine, brown, plume-like crystals, m. p. 200–203°. *Dinitrohexamethylacridine*, $(\text{C}_{19}\text{H}_{21}\text{N})\text{NO}_2$, yellow powder, m. p. 85–87°. *Tri-bromohexamethylacridine*,—



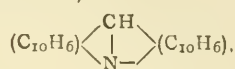
red. *Hexamethylacridine nitrate*, $(\text{C}_{19}\text{H}_{21}\text{N})\text{HNO}_3$, bright scarlet needles, m. p. 163–164° with decomposition. *Hexamethylacridine platinichloride*, $(\text{C}_{19}\text{H}_{21}\text{N})_2\text{H}_2\text{PtCl}_6$, scarlet needles. *Hexamethylacridine aurichloride*, $(\text{C}_{19}\text{H}_{21}\text{N})\text{HAuCl}_4$, yellow powder. *Hexamethylacridine mercurichloride*, $(\text{C}_{19}\text{H}_{21}\text{N})\text{HgCl}_2$, dark red, glistening needles with remarkable yellow lustre. *Hexamethylacridine dichromate*, $(\text{C}_{19}\text{H}_{21}\text{N})\text{H}_2\text{Cr}_2\text{O}_7$, deep red crystals. The sulphate, hydrochloride, and nitrite were also described, as was ethyl hexamethylacridinium iodide.

α -Naphthacridine,—



pale yellow crystals, m. p. 173°, sublimes, solutions

fluorescent. *Mononitro- α -naphthacridine*, $\text{C}_{21}\text{H}_{12}(\text{NO}_2)\text{N}$, m. p. 105–107°. *α -Naphthacridine platinichloride*, $(\text{C}_{21}\text{H}_{13}\text{N})_2\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$. *α -Naphthacridine picrate*, $(\text{C}_{21}\text{H}_{13}\text{N})\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, scarlet needles, m. p. 176–178°. *β -Naphthacridine*,—



yellow needles, m. p. 215·5°, sublimes, solutions fluorescent, identical with β -naphthacridine of Re-ed. *β -Naphthacridine platinichloride*, $(\text{C}_{21}\text{H}_{13}\text{N})_2\text{H}_2\text{PtCl}_6(\text{H}_2\text{O})_2$, yellow powder.

9. "The Polymerisation of Cyanic Acid: Cyanuric Acid and Cyamelide." By A. SENIER and T. WALSH.

In the polymerisation of liquid cyanic acid, cyamelide is not the only product. The two isomerides, cyamelide and cyanuric acid, are formed. These may be separated by treatment with water. Pure cyamelide so obtained is soluble in water to the extent of 0·01 per cent at 15°. The solubility of cyanuric acid at 15° is from 0·145 to 0·16 per cent. Phosphorus pentachloride has no action on cyamelide.

NOTICES OF BOOKS.

The Life of Pasteur. By RENÉ VALLERY-RADOT. Translated from the French by MRS. L. L. DEVONSHIRE. In Two Volumes. London: Archibald Constable and Co., Limited. 1902.

IN the "Life of Pasteur," by René Vallery-Radot, we have a work of more than usual interest, written by one in the position of closest intimacy. The title of the work has been fully substantiated; we have not merely a recapitulation of the labours of this truly great man, but we are brought into intimate acquaintance with the man himself. To English readers the thought might occur that the author with pardonable enthusiasm had introduced matters almost outside the bounds of the narrative, but the effect is only to enhance the interest in the work by giving an insight into French thoughts and customs that otherwise would only be realised by those who have had the privilege of experience in French scientific circles; in this way the reader is brought into close touch with such names as Biot, Ste. Claire Deville, J. B. Dumas, Regnault, and many others; even the chapter dealing with the war and the siege cannot be looked upon altogether as a digression, for it is legitimately introduced to bring out the extraordinary combination of science and patriotism found in this remarkable man. In studying the work the personality of Pasteur stands prominently before everything. Born in very humble circumstances, his father, a retired sergeant-major (though decorated with the ribbon of the Legion of Honour), carrying on the business of a tanner in the little town of Arebois, Louis Pasteur had to make his position in the world; fortunately his desire for a scientific career was encouraged by his father, but hard work, and plenty of it, was the road by which he had to travel, and the difficulty in the way only helped to stimulate a mind set upon success. There is a sentence in a letter from Pasteur, then a youth of eighteen holding the position of preparation master in the Royal College, Besançon, which is worth quoting:—"Three things, *will, work, success*, fill human existence; *will* opens the door, *work* passes the door, and at the end *success* comes to crown our efforts." Looking back fifty years afterwards he might well have summed up the whole of his labours with those three words.

As son, husband, and father, Pasteur seems to have had the share of trouble that falls to the lot of most mortals, but nothing could damp his insatiable desire to win

nature's secrets; the more difficult and dangerous the work the greater the delight in working, and yet he could never be charged with selfishness, but was ever ready to help and courteous to listen to both inquirers and critics; his modesty, depth of feeling, and religious convictions are related by the author with a simplicity that testifies of their genuineness; his oration at the funeral of his friend Ste. Claire Deville, and the kindness of heart that could keep him for a whole day at the bedside of a poor child who had been bitten by a mad dog, but not brought to him until too late for his treatment to take effect, and his tearful words to the father and mother, "and I did so wish I could have saved your little one," completely refute those fanatics who would brand him as a heartless vivisectionist.

The reality of his patriotism is shown, when in his young days he could place the whole of his savings of one hundred and fifty francs on the "autel de la patrie," and when later in life, in those dark days following the war, he refused a professor's chair at Pisa, with very great personal advantages, with "I should feel that I deserved a deserter's penalty if I sought away from my country in distress a material situation better than it can offer me." His feelings against his country's conquerors at that time were bitter indeed, and we find him writing to his pupil and friend M. Raulin, "every one of my future works will bear on its title-page 'Hatred to Prussia. Revenge! Revenge!'"—feelings that were softened but not altered, when, twenty years afterwards, he could courteously refuse the badge of the "Order of Merit" from the German Academy of Sciences.

Of Pasteur's long list of discoveries the first, and the one that brought him prominently before the scientific world, was his work on the optical properties and origin of tartaric and para-tartaric or racemic acid, and there is introduced a happy touch in the life of Biot, then seventy-four years of age. Biot having by careful personal verification satisfied himself of the genuineness of Pasteur's discovery, took the young man by the arm with the words, "My dear boy, I have loved science so much during my life that this touches my heart." But the greatest works of Pasteur began with his study of fermentations, and from that moment until the end of his life his labours are one unbroken record of triumphs; the study of the "infinitely small" brought results beyond the range of any human expectations; the settlement of the vexed question of spontaneous generation, a question beset with such difficulties that even his friend and patron Biot tried hard to stop him. "You will never find your way out," cried Biot; "I shall try," said Pasteur, and the result is a matter of history. The prevention of silkworm disease, treatment of splenic fever, puerperal fever, chicken cholera, the application of his discoveries to the antiseptic treatment in surgery, applied first with such wonderful success by Lister in England, and now universally in every hospital in the world; the investigation of rabies, with the treatment for hydrophobia and diphtheria, alone place Pasteur as one of the greatest benefactors of the human race; to him was granted the rare good fortune of living to reap in some measure the fruit of his labours. His hearty reception in the Academy of Sciences, gift of the Legion of Honour, substantial testimonial of gratitude from his countrymen, honours from every country in the world, must have helped much to lighten the bodily infirmity of his later years; but what must have appealed to the heart of the man more than any of these things was the thought of a "little Joseph Meister" saved from a death too horrible to contemplate, the life of the brave shepherd boy J. B. Jupille, women in lying-in hospitals, patients operated upon in hospitals and upon the battle-field, thousands of human beings whose existence had been saved by his methods—rewards of a far higher order than any social distinctions or recognition.

Science, said Pasteur, has been the "ruling passion in my life"; never before has the pursuit of science been so directly connected with the alleviation of human suffering.

Elementary Experimental Chemistry, Inorganic. Completely illustrated with Full-page Engravings of all the Apparatus and Chemicals used in Experiments. For Students in High Schools and Junior Classes in Colleges, and Private Learners. By W. F. WATSON, A.M., Professor of Chemistry and Biology in Furman University, South Carolina. New York: A. S. Barnes and Co. 1901.

THE author has succeeded in his endeavour to "present the fundamental principles of elementary chemistry in a brief, clear, and logical manner," and throughout the work no pains have been spared by the author to make his meaning clear. A novel feature in the book is the introduction of each subject by a full-page illustration from a photograph of the apparatus and materials to be used in the experiments about to be described; this is quite a new departure, and is the outcome of the desire to save labour both to the instructor who is using the work and to the student. We must confess to the feeling that both by this device are in a way reduced to the level of automata, and it does not tend to "develop the observing and reasoning faculties" of either. Some of these full-page engravings, although doubtless possessing artistic merit, have but little connection with the subject; for instance, "The Metals" is introduced by a picture of some shelves, with a hammer, some photographic dishes, a very fine rack of test-tubes, and a number of bottles apparently partly full of something, but with labels unreadable. However, as we have already pointed out, the subject matter is simple, clear, and to the point, and this is of the most importance. We are glad to see that in the list of elements didymium has been eliminated, and neo- and praseodymium introduced. There is an appendix containing much useful information and tables, including an extremely useful one of the solubilities of metallic salts. The book is well indexed, and has a table of contents.

The Laboratory Companion to Fats and Oils Industries. By Dr. J. LEWKOWITSCH, M.A., F.I.C. London: Macmillan and Co., Limited. New York: The Macmillan Company. 1901.

THIS book consists almost exclusively of tables. For explanations and description of methods the reader is referred to the author's "Chemical Analysis of Oils, Fats, and Waxes, and of the Commercial Products Derived Therefrom" (Second Edition, Macmillan and Co., 1898). A few pages of subject matter are added explanatory of the system of testing oils and fats from results of more recent date than the work on chemical analysis. Many of the tables and values extracted from the author's laboratory note-books are now published for the first time.

This collection of tables and data will undoubtedly be of considerable value to the works chemist. There is a table of contents and a very complete index.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—Dr. A. Wynter Blyth's fear that the Council of the above body will "cease to be respected" has, I am afraid, good justification, and on other grounds than that mentioned in his letter to the CHEMICAL NEWS of January 24th.

Judging from the frantic efforts of the Council to draw the Associates within the fold of the Fellowship, they must have grave fears that something like 80 per cent of the Associates do not think it worth while to proceed to the higher qualification. If this is so it is surely an in

dication that something is wrong, and it is high time the members took more interest in the doings of the Council, and insisted upon the object of the incorporation being carried out. If the Institute is to remain merely an examining body why accumulate funds? What has it done to raise the status of the chemical profession? I am aware that some half-hearted effort was made to secure legal recognition, but still the fact remains that it has accomplished nothing but a satisfactory balance-sheet and a club-house for the London members.

Surely with the ample funds and income at its disposal it can now do something towards the object of its existence without extorting further guineas from not too well off Associates.

Let the Institute do something to justify confidence in it, and the Associates will be eager enough to proceed to the Fellowship; but to charge four or five guineas for changing the letter A to F (for that is all it amounts to), is a trifle arbitrary even if it is not illegal.

"Hope deferred maketh the heart sick." The Institute has now been in existence for twenty-five years, and during the past seventeen years with a Royal Charter. Yet it has no journal or other organ; it has no provincial library, it gives no certificates of competency, it has done nothing to advance the well-being of the members, legally, professionally, socially, or benevolently; truly a more miserable record of inactivity and failure it would be hard to find.—I am, &c.,

AN ASSOCIATE.

Liverpool, February 3, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 2, January 13, 1902.

Preparation and Properties of Sodium Hydride.—Henri Moissan.—Sodium, like potassium, gives a crystalline hydride of formula NaH, which possesses most energetic reducing properties and is soluble in the alkaline metals. This substance is prepared by slowly raising the temperature of sodium in an atmosphere of hydrogen gas. The hydride thus prepared is in the form of transparent crystals, which are decomposed by slight traces of water. The existence of this new compound shows that the alkaline metals, as well as the metals of the alkaline earths, can be made to unite with hydrogen directly, to give perfectly crystalline and definite compounds, decomposable by water, and more or less dissociable by simple elevation of temperature. These form a new series of curious compounds possessing important properties.

Radio-active Bodies.—P. Curie and Mme. S. Curie.—During their extensive researches on the subject of radio-active bodies, the authors admit that the radio-activity is an atomic property of the body. Each atom of such a body acts as a constant source of energy. From this hypothesis very varied consequences can be deduced, which can be confirmed by experiment without the necessity of definitely deciding from whence this energy is obtained. The experience of several years shows that for uranium, radium, thorium, and probably also for actinium, the radio-activity is rigorously the same whenever the body is brought to the same chemical and physical state, and this activity does not vary with time.

Preparation and Properties of Strontium Hydride.—Henri Gautier.—Strontium hydride, whose existence has already been announced by the author, is found to be a reducing agent. From its composition, and from a study

of its properties, it apparently is very similar to calcium hydride, CaH_2 .

Chemical Equilibrium of Iron-carbon System.—Georges Charpy and Louis Grenet.—A study of various specimens of iron-carbon metal leads the authors to the following conclusions:—(1) The separation of graphite proceeds to a temperature considerably lower than that at which the retention of silicon is the greatest. (2) The separation of graphite, once begun, continues to temperatures below those at which the reaction could be started. (3) At a constant temperature the separation of graphite is effected progressively with a rapidity which decreases as the temperature is lowered and as the retention of silicon becomes more feeble. (4) The dissolved graphite which is present at equilibrium point appears only to depend very slightly on the quantity of silicon present. (5) The dissolved graphite corresponding to equilibrium point increases when the temperature is lowered, and at low temperatures the equilibrium appears to correspond to the absence of combined carbon.

Addition of Mixed Organo-Magnesium Compounds on Trioxymethylene. Syntheses of Primary Alcohols.—V. Grignard and L. Tissier.—Whilst free aldehydes react with great energy on organo-magnesium compounds, trioxymethylene only depolymerises slowly in contact with these substances; the reaction is scarcely perceptible and prolonged heating is necessary. Using special precautions the authors obtain excellent yields, and prove that in the aromatic series, as well as in the fatty series, a certain number of syntheses of primary alcohols are possible, which fact testifies to the generality and practical value of the use of organo-metallic compounds.

Preparation and Properties of Imido-dithio-carbonic Ethers.—Marcel Delépine.—In a previous research the author described the methods of formation of the imido-dithio-carbonic ethers $\text{RN}=\text{C}(\text{SR})_2$, and justified their constitution by their synthesis, their oxidation, their reduction, and their decomposition. He now describes a more definite preparation, and examines the properties of this compound.

The Inversion of Saccharose.—P. Petit.—The heat evolved by the inversion of saccharose can be deduced from the heats of combustion and solution. The author endeavours, however, to determine this quantity directly for dissolved saccharose by using sulphuric acid. As a mean of a number of experiments he finds that the heat evolved by the inversion of a gramme-molecule of saccharose dissolved in 140 molecules of water is 2639 cal. at 58.5°, and 2675 cal. at 63°. The author proposes to repeat these experiments with sucrose, and to apply the same method to an examination of the products of saccharification of amidon by amylase.

The Solubility of Bicalcic Phosphate in Pure Water.—A. Rindell.—The constants of solubility of different phosphates of lime being very incomplete and even contradictory, the author undertakes an investigation of this subject with modern methods. He uses a very pure salt, finely pulverised, and having the following composition:— CaO , 32.70; P_2O_5 , 41.30; H_2O , 26.20 per cent. The numbers obtained show clearly (1) that the concentration of the solution increases with the time and the mass of the salt in contact with a given volume of water; (2) the quantity R at first differing but slightly from unity increases with the concentration.

The Methods of Volumetric Estimation by Stannous Chloride of Copper, Iron, Antimony, Powdered Zinc, Sulphur in Sulphides, Glucose, and Sugar.—F. Weil.—The author found some years past that instead of effecting the above titrations at boiling-point, they could be equally well performed at ordinary temperatures. It is necessary to introduce 10 c.c. of the solution to be titrated to 30 c.c. of hydrochloric acid and some fragments of white marble. The carbon dioxide which is evolved prevents the oxidation of the cuprous chloride produced

during the reaction. The advantage gained by working at ordinary temperatures is the absence of hydrochloric vapours, which are evolved in great quantity when the solutions are treated at boiling-point.

Mechanism of Synthesis of Leucine Isomer.—A. Etard and A. Vila.—Leucine which is derived by the synthesis of amylic alcohol is different from biological leucine. It is formed as a result of a series of reactions which can be controlled. The leucine of synthesis possesses two asymmetric carbons, and when it is decomposed certain actions take place on the cellulose which ordinarily do not occur.

MISCELLANEOUS.

Institute of Chemistry Examinations.—Pass Lists (January, 1902).—*Intermediate Examination*: G. J. Alderton; K. B. Benham; J. L. Garle; H. W. Hill; J. Johnston; A. W. Knapp, B.Sc. (Birm.); S. G. Paine; W. B. Parker; J. B. Pursglove; J. C. Sheldon; H. A. Tempamy; and R. Tyler. *Final A.I.C. Examination (Branch "A," Mineral Chemistry)*: A. G. Armstrong; W. W. Lumsden; A. B. Shepherd, B.Sc. (Vid.); and W. F. Sutherst, Ph.D. (Geneva). *Branch "D" (Organic Chemistry)*: G. Clarke, jun.; E. D. M. Neuman, B.A. (Oxon.); Ph.D. (Göttingen); H. A. D. Neville, B.Sc. (Lond.); G. M. Norman, A.R.C.Sc., B.Sc. (Lond.); W. H. Nuttall; W. H. Peters, and V. W. Theobalds. *Branch "E" (Analysis of Food and Drugs, including an Examination in Therapeutics, Pharmacology, and Microscopy)*: F. W. F. Arnaud; J. Evans; J. E. Jenkins; W. Partridge; S. O. Richmond; and E. C. Spurge.

Prize for Industrial Hygiene.—The Council of the Society of Arts are prepared to award, under the terms of the Benjamin Shaw Trust, a Gold Medal, or a prize of £20. The Medal, under the conditions laid down by the testator, is to be given "for any discovery, invention, or newly-devised method for obviating or materially diminishing any risk to life, limb, or health, incidental to any industrial occupation, and not previously capable of being so obviated or diminished by any known and practically available means." Intending competitors should send in descriptions of their inventions not later than May 1, 1902, to the Secretary of the Society of Arts, Adelphi, London, W.C. Such descriptions may be sent in under the inventor's name, or under a motto, accompanied by a sealed envelope enclosing the name as preferred. The Judges will be appointed by the Council. The Council reserve the right of withholding the prize or of awarding a smaller prize or smaller prizes, if in the opinion of the Judges nothing deserving the full award is sent in.

MEETINGS FOR THE WEEK

MONDAY, 10th.—Society of Arts, 8. (Cantor Lectures). "Personal Jewellery from Prehistoric Times," by Cyril Davenport.

TUESDAY, 11th.—Royal Institution, 3. "The Cell—its means of Offence and Defence—Immunity," by Allen Macfadyen, M.D., B.Sc.

WEDNESDAY, 12th.—Society of Arts, 8. "Industrial Redistribution and its connection with the Overcrowding Question," by W. L. Madgen.

THURSDAY, 13th.—Royal Institution, 3. "The Scot of the Eighteenth Century—II., In Kirk," by the Rev. John Watson, D.D. (Ian MacLaren).

FRIDAY, 14th.—Royal Institution, 9. "Magic Squares and other Problems on a Chess Board," by Major P. A. MacMahon, R.A., D.Sc., F.R.S.

— Physical, 5. (Annual Meeting). Address by the President. Mr. T. H. Littlewood will exhibit an Atwood's Machine.

SATURDAY, 15th.—Royal Institution, 3. "Some Electrical Developments," by Lord Rayleigh, M.A., F.R.S., &c.

EAST LONDON TECHNICAL COLLEGE.

The following **DAY COURSES** of Studies are now being held, viz.:—

MATHEMATICS. J. L. S. HATTON, M.A. and W. F. S. CHURCHILL, M.A.
PHYSICS. R. A. LEHFELDT, D.Sc.
CHEMISTRY. J. T. HEWITT, D.Sc.
ENGINEERING (Mech.) . . . D. A. LOW, M.I.M.E.
ENGINEERING (Elec.) . . . J. T. MORRIS, A.Inst.C.E.

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BOROUGH OF SOUTHWARK.

APPOINTMENT OF ASSISTANT TO THE PUBLIC ANALYST.

The Council are prepared to receive Applications for the Post of ASSISTANT to the PUBLIC ANALYST from persons not exceeding thirty-five years of age. The salary will be £100 per annum, rising by annual increments of £10 to £130 per annum. Preference will be given to candidates who have had previous experience in the Laboratory of a Public Analyst.

The person appointed will be required to devote the whole of his time to the services of the authority, and there will be no pension or superannuation allowance.

Applications, on forms which may be obtained at my office, stating age, experience, and qualifications, and accompanied by not more than three testimonials, to be sent to me, endorsed "Assistant," not later than 4 o'clock on MONDAY, FEBRUARY 17th, 1902.

Canvassing will disqualify.

Southwark Town Hall,
Walworth Road, S.E., February 5, 1902.

J. A. JOHNSON,
Town Clerk.

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Berichte der Deutschen Chemischen Gesellschaft in Berlin, 1875-97. 38 vols. half calf, remainder in parts. £28.

Cavendish Society Publications. 30 vols. £10 10s.

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Chemical News, complete, 1860-98. 78 vols., orig. cloth. £22 10s.

Chemical Society Journal, 1888-1900. 20 vols. half cloth, remainder in parts. £10 17s. 6d.

Jahresbericht über die fortschritte der Chemie, 1859-71, and 1874-83. Register, 1867-76. 24 vols. £15 15s.

Chemistry Applied to Manufactures and Art. 8 vols., 1880. 25s.
Spon's Encyclopædia of the Industrial Arts. 2 vols., 1882, half morocco. 55s.

Dumas' Traite de Chimie Applique aux Arts, with Atlas. 9 vols. 1828. 30s.

Textile Colourist, edited by O'Neil. 4 vols., 1876-7. 40s.

Pelouse et Fremy's Traite de Chimie Générale. 7 vols. 25s.

Year-Book of Pharmacy, 1870-96. £4 4s.

Pharmaceutical Journal and Transactions, 1841-99. 62 vols. £11.

Watts' Dictionary of Chemistry. 4 vols. £4 18s. 6d.

Thorpe's Dictionary of Applied Chemistry. 3 vols. £4 2s. 6d.

I am always ready to purchase odd Vols. or Nos.—*Chemical News*, 1860-70; *Chemical Society Journal*, any before 1865; *Analyst*, 1876-90; *Chemical Industry Journal*, 1882-3.

EXPERIENCED VALUERS sent to any part of Great Britain to value Scientific Libraries.

THE CHEMICAL NEWS.

VOL. LXXXV., No. 2203.

THE SPECIFIC VOLUMES OF OXYGEN AND NITROGEN VAPOUR AT THE BOILING-POINT OF OXYGEN.*

By JAMES DEWAR, M.A., D.Sc., LL.D. F.R.S.,

In my paper on "The Boiling-point of Liquid Hydrogen Determined by Hydrogen and Helium Gas Thermometers" (*Roy. Soc. Proc.*, 1901, vol. lxviii.; *CHEMICAL NEWS*, vol. lxxxiii., p. 97) it was pointed out that a constant-volume gas-thermometer filled with oxygen gas, having a pressure at 0° C. of about 800 m.m., gave a very accurate value of the boiling-point of liquid oxygen. As it seemed advisable to confirm this result indirectly, an attempt was made to determine the vapour-density of oxygen at its boiling-point by direct weighing, the intention being, if the experimental results proved at all encouraging, to repeat the work on a larger scale and with greater precautions. As at present there is no likelihood of my being able to undertake the more accurate determinations, the results of the preliminary enquiry are presented to the Society. They give in any case, with considerable accuracy, the specific volumes which have never been directly determined.

In order to obviate any question of the buoyancy of the air, two flasks, A and B, of as nearly as possible the same air displacement, were counterpoised on an Oertling balance. The B flask remained permanently on one scale of the balance during all the weighings, while the A flask was weighed either exhausted or filled with oxygen (or nitrogen), under various circumstances according as the experiments required.

As the flask cooled in the liquid oxygen or air had to stand an internal pressure of from three to four atmospheres, it was considered expedient to select a spherical vessel of about 300 c.c. capacity, to which was sealed a narrow tube having a very carefully ground stopcock at its end. Preliminary experiments were made to determine the change of volume of the flask when subjected to internal pressure. The flask, filled with air at five atmospheres pressure, was left for twenty-four hours with the stopcock closed, without showing any leakage. To determine the effect of pressure on the capacity of the flask, it was filled with water under one atmosphere pressure, and again with water under three or four atmospheres pressure (which included the range of the observations) and the weights noted. From these the coefficient of expansion of the flask was found to be 0.000306 per atmosphere excess of internal over external pressure. The temperature coefficient of expansion of glass (cubical) was taken to be 0.000025, which for a variation of temperature of some 200° altered the capacity of the flask by about 1.5 c.c. The content of the flask up to a fixed mark on the neck below the stopcock was determined to be 315.973 c.c. at 17° C.; the content between the mark and the stopcock was determined both by measurement and by the weight of mercury it contained, and was found to be 0.127 c.c.

Before each experiment the A flask, filled with the gas under observation, was exhausted to a pressure of from 2 to 4 m.m. of mercury (which was afterwards involved as a correction in reducing the observations) and weighed, the weight a which had to be added to its scale pan to balance the B flask being noted. The A flask was then filled with carefully purified oxygen (or nitrogen), and the

temperature of the flask and contents (still in communication with the gas reservoir) was lowered by immersing it up to the mark in liquid oxygen (or air) until the gas ceased passing into the flask, and the pressure was finally equalised to that of the atmosphere. This is really the most important part of the manipulation, as the accuracy mainly depends on giving sufficient time to the cooling, while at the same time taking care to avoid any excess of pressure that would necessarily lead to liquid condensation on the glass surface. During the rapid inrush of gas, it is advisable to keep the pressure well below that of the barometer at the time, and to finally adjust the pressure at the end of the absorption. The vessel containing the liquid oxygen had a cardboard cover which crossed the neck of the flask at the mark, thereby preventing the cooled vapour of the oxygen from freezing the stopcock. The remaining portion of the tube between the mark and the stopcock, namely, 0.127 c.c., was therefore approximately at the temperature of the room. When the temperature of the flask and its contents became stationary the stopcock was closed, the flask removed, and after heating up to the temperature of the room, weighed against the B flask and any further necessary counterpoise b . The weight of oxygen vapour in the flask at its boiling-point was thus equal to $a+b$, subject to the corrections which have been indicated.

To the five sources of error or correction indicated above, there remains to be added that due to additional buoyancy of the air during the weighing of the flask, when filled with oxygen at its boiling-point, for these weighings were made at the temperature of the room, which would cause a rise of pressure in the flask and therefore expansion of its volume. But this error was so small that it could safely be neglected.

As the intention was not only to ascertain the density of oxygen and nitrogen at their respective boiling-points under atmospheric pressure, but also under diminished pressure, experiments were made with nitrogen at ordinary temperatures and at pressures varying from about one-sixth of an atmosphere to ordinary pressures, in order to find the range of variation in the results with the 316 c.c. flask to be used in the subsequent low temperature experiments. In Table I. are details of these observations, and the results reduced according to the ordinary gaseous laws.

In reducing these observations the following corrections were involved.—A correction of 0.0015 grm., due to imperfect exhaustion of the flask A while being weighed as empty; the correction due to the neck of the flask between the mark and the stopcock was negligible; the volume of the flask when corrected for temperature was 315.973 c.c., and when it was necessary to correct further for excess of external over internal pressure, the values were as given in Column V; in the last four experiments this correction varied from about 0.059 to 0.073 c.c.

The first three experiments give a mean value of 1.260 grms., at standard temperature and pressure, as the weight of a litre of nitrogen. This is about a quarter per cent higher than the accepted value of 1.257. The extreme variation in the individual experiments is about half a per cent. The average value of the results under about one-third of an atmosphere is 1.266 grms.; the tendency under the low pressures being to make the density half a per cent higher. Considering that in the actual low-temperature experiments the mass of gas to be weighed would be at least three times greater, it was inferred that in spite of difficulties of manipulation and corrections the results might be anticipated to lie within a half per cent of the true value.

Table II. gives the results of six experiments made on the density of the vapour of oxygen at its boiling-point taken as 90.5° absolute, and under atmospheric pressure, where p , p_1 , T_1 , a , b , are the same symbols as used in the previous table, d is the calculated density at 90.5° absolute and 760 m.m., and v is the specific volume $1/d$.

In these reductions the following corrections were in-

* A Paper read before the Royal Society, January 30, 1902.

TABLE I.—Density of Nitrogen, Ordinary Temperature.

No.	p_1 . M.m.	T_1 . °	p . M.m.	a. Grm.	b. Grm.	V.	d.	d_0 .
1.	742°0	15°5	742°0	0·37	—0°0022	315°973	0°001168	0°001265
2.	742°0	15°5	742°0	0·3668	—0°001	315°973	0°001162	0°001258
3.	742°0	16°0	742°0	0·367	—0°0015	315°973	0°001161	0°001259
4.	751°0	16°5	281°3	0·371	—0°2328	315°913	0°000442	0°001265
5.	751°0	16°5	284°2	0·371	—0°231	315°913	0°000447	0°001269
6.	751°0	17°0	268°5	0·371	—0°239	315°911	0°000422	0°001269
7.	753°0	17°5	176°2	0·3705	—0°2850	315°899	0°000275	0°001262

Where p_1 = barometric pressure at the time of observation,

T_1 = temperature of the room at the time of observation,

p = pressure of the nitrogen vapour in the flask during the experiment,

a, b = as defined before,

V = the volume of the flask corrected for temperature and compression,

d = the calculated density at T_1 ° and pressure p ,

d_0 = the value of d reduced to 0° and 760 m.m. by the ordinary gaseous laws.

TABLE II.—Density of Oxygen Vapour at its Boiling-point.

No.	$p=p_1$. M.m.	T_1 . °	a. Grm.	b. Grm.	d.	v.
1.	775°5	15°5	0·388	1°0225	0°004402	227°15
2.	770°3	16°5	0·3865	1°015	0°004403	227°07
3.	771°0	17°5	0·3875	1°0245	0°004432	225°60
4.	771°8	17°5	0·3875	1°0260	0°004432	225°59
5.	775°0	16°0	0·388	1°028	0°004422	226°12
6.	774°2	16°5	0·3875	1°028	0°004425	225°97

TABLE III.—Density of Oxygen Vapour at its Boiling-point under Diminished Pressure.

No.	p_1 . M.m.	T_1 . °	p . M.m.	a. Grm.	b. Grm.	V.	d.	v.
1.	741°8	18°5	287°0	0·3695	0°1315	314°340	0°001588	625°74
2.	741°8	18°5	281°5	0·3695	0°1345	314°339	0°001607	622°01
3.	746°5	20°0	279°0	0·3690	0°1290	314°338	0°001588	629°41
4.	746°5	20°0	310°2	0·3690	0°1880	314°342	0°001776	562°95
5.	746°5	19°0	159°4	0·3690	0°0850	314°323	0°000907	1101°46

TABLE IV.—Density of Nitrogen Vapour at the Boiling-point of Oxygen.

No.	$p=p_1$. M.m.	T_1 . °	a. Grm.	b. Grm.	d.	v.	T. °
1.	771°8	17°5	0·3875	0°8555	0°0039021	256°27	(90°5)
2.	773°0	17°0	0·385	0°8555	0°003885	257°39	(90°5)
3.	777°2	16°0	0·3885	0°9575	0°004192	238°53	84°05
4.	777°3	16°5	0·3885	0°9500	0°004168	239°90	84°54
5.	777°3	16°5	0·3885	0°942	0°004143	241°34	85°04
6.	777°3	16°5	0·3845	0°9235	0°004073	245°49	86°50

volved:—0°002 grm. due to imperfect exhaustion of A flask while being weighed as empty; 0°0002 grm. due to the contents of the neck of the flask between the mark and the stopcock not being at 90°5°; the volume of the flask up to the mark contracted at 90°5° to 314°398 c.c.; no correction was necessary for compression.

Thus the mean weight of 1 litre of oxygen vapour at 760 m.m. and 90°5° absolute is 4°420 grms., and the specific volume is 226°25 c.c. If the first two experiments are eliminated on the assumption that the proper equilibrium of temperature had not been attained, the average weight per litre would become 4°428 grms., and the specific volume 225°82.

Taking Regnault's density of oxygen at 0° and 760 m.m., the density at 90°5° in the ordinary way would be 0°0043137, and the specific volume 231°82 c.c. Thus the volume given by the ordinary gaseous laws is 1°0246 times the average observed volume; or we may put it that p_v is diminished at the boiling-point of oxygen by 2°46 per cent. Again, while the ratio of the absolute temperatures is 3°017, the ratio of the densities is 3°091.

Behn (*Ann. der Physik.*, vol. i., 1900, "Sublimationswärme der Kohlensäure und die Verdampfungswärme der Luft") has determined by an indirect method the specific volume of oxygen, and finds the value 358, which is nearly 60 per cent greater than the volume found by the direct method. The mode of procedure he adopts is to ascertain

directly three quantities out of four in the ordinary thermodynamic equation, correlating latent heat, temperature, increment of pressure to temperature, and specific volume, thereby deducing the unknown quantity. Now, of the three experimental values required, one, viz., increment of pressure to temperature, can only be got by calculation from the vapour-pressure curve, and much depends upon the accuracy of this value. Accepting Estreicher's vapour-pressures for liquid oxygen below its boiling-point as the most reliable, a Gibbs equation gives the increment per degree near 740 m.m. pressure as 78°67 m.m. mercury pressure, or 106°93 grms. per square c.m. This value, taken along with the latent heat found by Behn, and the boiling-point, gives, when inserted in the thermodynamic equation, a specific volume of 223°55, which is within less than 2 per cent of the value found by the direct-density determinations.*

Further experiments were made on oxygen vapour at 90°5° and under reduced pressures. These experiments

* In the same way Behn's specific volume of carbonic acid would be contradictory of my proof that a constant-volume gas-thermometer filled with carbonic acid at about atmospheric pressure gives a very accurate value of its own boiling-point. Assuming the ordinary gaseous laws, the specific volume ought to be 361°6 instead of 423 given by Behn. Now my value of the increment of pressure to temperature at the boiling-point is 62°84 m.m. mercury pressure, and this, along with the values used by Behn in the thermodynamic equation, gives 363 as the specific volume. This comes much nearer the anticipated value of the constant.

and their results are given in Table III. The same symbols are used as in the preceding tables, except that d is the calculated density at 90.5° absolute and pressure p , and v is $1/d$. The corrected volume of the flask is entered under V .

In reducing these observations the following corrections were involved:—A correction of 0.0014 gm. to 0.0015 gm. due to imperfect exhaustion of the A flask while being weighed as empty; the correction due to the neck of the flask between the mark and the stopcock not being at 90.5° amounted to 0.00003 , 0.00007 gm., and was practically negligible; the volume of the flask, which, when corrected for temperature, was 314.398 c.c., had to be further corrected for excess of external pressure over internal pressure by amounts varying from 0.0551 c.c. to 0.0742 c.c. If the first three experiments are averaged (the pressures being so near), the weight of a litre of oxygen at 90.5° absolute under a pressure of 282.5 m.m. would be 1.5982 grms. The ratio of this density to the value previously found for one atmosphere pressure, viz., 4.42 grms., is 2.765 , and the ratio of the pressures is 2.690 . It appears that the ratio of the change of density of the vapour of oxygen at 90.5° absolute, under variable pressure, is greater than the ratio of the change of pressure. It is clear, however, that it would be necessary to work upon a larger scale in order to get satisfactory vapour densities at low temperatures under pressures below that of the atmosphere.

Table IV. gives the observations on the density of nitrogen vapour at the boiling-points of liquid oxygen and liquid air respectively; the first two were made in oxygen, the last four in air. The symbols used are the same as before, except that d is the calculated density at T° absolute and 760 m.m., and v is $1/d$.

In reducing these observations, the following corrections were involved; a correction of 0.002 gm. due to imperfect exhaustion of the A flask, while being weighed as empty; the correction due to the neck of the flask between the mark and the stopcock not being at temperature T amounted to 0.00014 gm., and was practically negligible; the volume of the flask, which only required to be corrected for temperature, was 314.398 c.c.

Experiments 1, 2 were made with liquid oxygen taken to be at temperature 90.5° absolute. The experiments 3, 4, 5, 6 were made in one and the same sample of liquid air, with rising temperature. For these temperatures, obviously only a few degrees below the boiling-point of oxygen, the ordinary gaseous laws may be held to apply, in order to determine their values. Thus we may employ the formula—

$$T = v \frac{90.5}{256.833}$$

where 256.833 is the mean of the volumes of Nos. 1, 2, to get the temperature of the last four experiments. The values thence obtained are entered in column T.

The first two experiments made with liquid oxygen give a ratio of the nitrogen densities from my own values of 3.088 , the absolute temperature ratio being 3.017 ; my values for the ratio of the oxygen densities for the same range of temperature being 3.091 as previously deduced. We may safely assume that if the density of nitrogen were observed at its boiling-point it would deviate as much from the ordinary gaseous laws as oxygen. Further, the specific volume of nitrogen at its boiling-point of 78° absolute would from the above formula be 221.3 as compared with 226.2 , the similar value found for oxygen.

The general inference to be drawn from these preliminary experiments is that reliable vapour densities may be determined at very low temperatures. There seems to be no reason why the vapour density of hydrogen at its boiling-point should not be accurately ascertained; only, as in this case the internal pressure in the weighing flask would amount to nearly 15 atmospheres, it would be advisable to construct the flask of some metal or alloy. A flask of the size used in the oxygen experiments filled

with the vapour of hydrogen at its boiling-point would be equivalent in weight to between 4 and 5 litres of hydrogen at the ordinary temperature and pressure, and such an amount of material ought to give density results at the boiling-point of hydrogen of considerable exactness, notwithstanding the great manipulative difficulties that would necessarily be involved in the execution of such a determination at 21° absolute.

IMPROVED ELECTRIC FURNACE FOR LABORATORY USE.

By SAMUEL AUCHMUTY TUCKER
and
HERBERT R. MOODY.

ELECTRIC furnaces hitherto described have been found by the writers to possess certain disadvantages for experimental purposes. This led them to devise the form of furnace herein described which it is thought is a convenient piece of apparatus to build, and will be found to be well adapted to a variety of work in the laboratory.

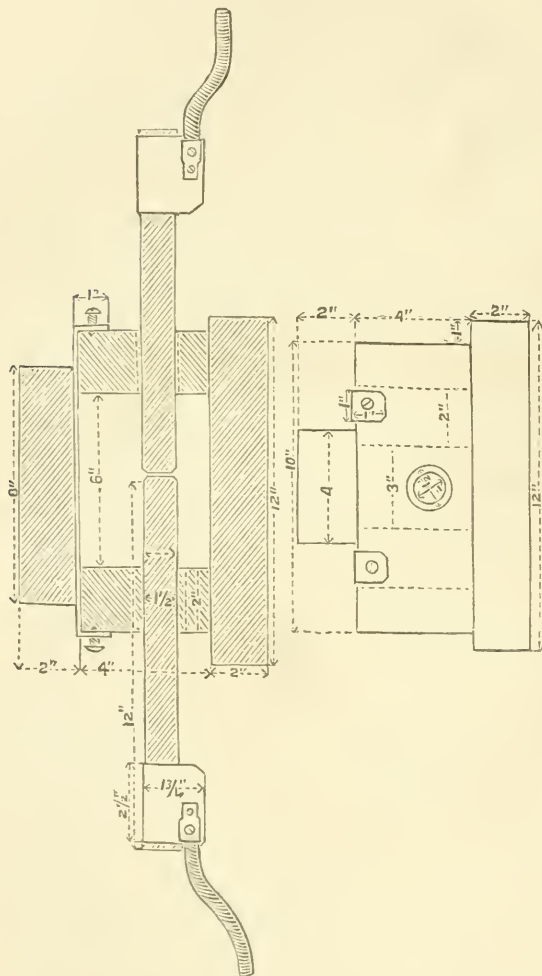
The Moissan type of furnace is now well known to every one, but it is troublesome in several ways. If built from chalk blocks in the rough, it takes both skill and time to cut them to the exact form required; it is then necessary to dry the blocks very thoroughly, otherwise they will crack in all directions, and render the furnace useless immediately. A perfectly dry furnace supported by metallic bands will generally crack to some extent, and it is seldom possible to put the furnace in use a second time. The form of furnace described by one of us (*American Electrician*, xi., 408), which simply consists of a graphite crucible forming one pole, the other being a carbon rod supported vertically with an arrangement for raising and lowering it at will, is useful for some purposes, but there is too much exposure to the air for many operations, and the material of which the crucible is composed is likely to introduce undesirable impurities during the fusion. The operator is exposed to very intense radiant heat, which interferes considerably with its use for any lengthened period. The present form of furnace is after the Moissan type, and is composed of carbon bricks 12 inches by 4 inches by 2 inches, luted together with Dixon stove paste. The sides of the furnace were of 6-inch brick, thus making a working space of about 6 by 4 by 2 inches. This space could, of course, be increased or diminished at will according to the charge used. The whole was then clamped, and held firmly together by iron cross bars provided with adjusting screws at each end, these bars being insulated from the body of the furnace by strips of asbestos. The end bricks were perforated with 1.5-inch holes containing a collar of asbestos or a small cylinder of clay, through which the electrodes of carbon passed (1 inch by 12 inches) into the furnace chamber. Connection was made with these electrodes by copper sleeves lined with copper gauze, and tightened with set screws, which at the same time carried copper lugs which held the flexible cables.

The tendency to overheat those portions of these electrodes outside of the furnace, and consequent wasting away, and also the tendency to melt the copper connections, was overcome by either one of two expedients; that is, by the use of the water-jacket, or by heavily copper-plating the carbons. This latter did not furnish quite as perfect a protection, but it was somewhat less troublesome than the former, and was, consequently, the one most used.

The construction of this furnace gives it considerable durability; so much so is this the case, that only three sets of brick were used throughout the year, in which almost a hundred runs were made. The greatest deterioration comes from the oxidation of the outer surface of the carbon bricks, and this could be largely avoided by a suit-

able covering of fire-bricks. Frequently ten or twelve runs could be made without dismantling the principal parts, and the substitution of new asbestos collars serves to make everything ready for the next run.

In this type of furnace the desired current may be readily maintained throughout the entire fusion, and this is not easily done with a crucible furnace where variations are unknowingly introduced by the constantly changing distance between the poles. This form of furnace may be used with double arc on 110 volt circuit with considerable economy. For example, with a single arc furnace and with a polar separation of 18 m.m. and enough resistance in circuit, the following reading was obtained:—125 ampères, 70 volts, and, consequently, 8750 watts.



These should be compared with the following results obtained while using the double arc furnace. Here all the resistance was cut out, and then the instruments showed 175 ampères and 90 volts. A few moments after this the reading was 125 ampères, and 100 volts or 12,500 watts.

The only difficulty in using this type is to prevent the extinction of the arcs, but that trouble is far from insurmountable. The dimensions given for the furnace are suitable for currents up to 300 ampères, at 70 volts. For work requiring more power than this it is necessary to increase the size throughout and use electrodes of 2-inch diameter.

If the luting has been carefully done the furnace will be

sufficiently gas-tight to permit a fusion to be carried on in an atmosphere of any desired gas, the gas being introduced through an annular electrode. This furnace is adapted to almost all kinds of fusion processes, and has been used in the greatest variety of work.—*Journal of the American Chemical Society*, xxiii., No. 7.

NOTE ON SOME MODIFIED FORMS OF PHYSICO-CHEMICAL MEASURING APPARATUS.*

By ALLERTON S. CUSHMAN.

A. A Convenient Arrangement of the Kohlrausch-Ostwald Conductivity Cell.

In working with the usual form of Kohlrausch-Ostwald conductivity cell the writer has experienced some difficulty in arranging the electrodes so that they may be easily adjusted at any required distance one from the other, while, on the other hand, when once set to a position the constant for the cell may be depended upon. The growth of physico-chemical methods of investigation has been so sudden that the manufacturers of instruments of precision

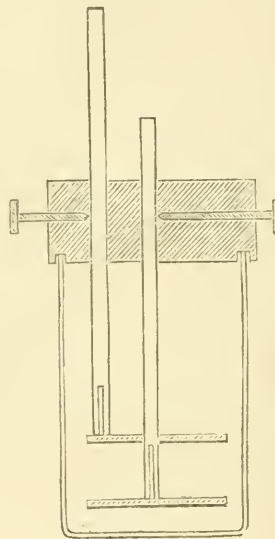


FIG. 1.

have not kept pace with the requirements of modern research. The physical chemist, therefore, has been obliged to depend largely on "home-made," and too often very imperfect, apparatus. It is not uncommon in many laboratories to see this important and delicate measuring instrument arranged in such a way that the electrodes are most insecurely fastened into place by means of splashes of sealing-wax, or, as is the case with the cells ordinarily supplied by the dealers, the mere friction of the glass supports of the electrodes against the holes in the ebonite cover through which they pass, is depended upon to insure the constancy of the cell.

In Fig. 1 of the accompanying illustrations is shown an arrangement of the cell which very admirably meets every requirement. The glass tubes into which the electrodes are fused fit snugly, but without binding, the holes in the heavy ebonite cover, which is in cross-section in the cut. The brass set-screws as shown are furnished with ebonite

* Contribution from the Chemical Laboratory of Bryn Mawr College. From the *Journal of the American Chemical Society*, xxiii., No. 7.

tips, which bear gently on the glass supports and remove the danger of contamination of the electrolyte by any accidental wetting of the screw points. A cell of this description which has been in frequent use for more than a year has not changed its constant. The electrodes are made of platinum, of nearly a millimetre in thickness, and are secured to the glass supports with such care that they are quite immovable.

B. On a Modified Form of the Ostwald Burette-Calibrator.

The usual Ostwald burette-calibrator has the general form shown in Fig. 2, without the etched scale upon the pipette stem. It is calibrated to deliver exactly 2 c.c. between two etched marks, and the deviations of the burette scale from the truth are then found by a series of deliveries from the pipette. The initial standardisation of the pipette requires a number of careful and difficult

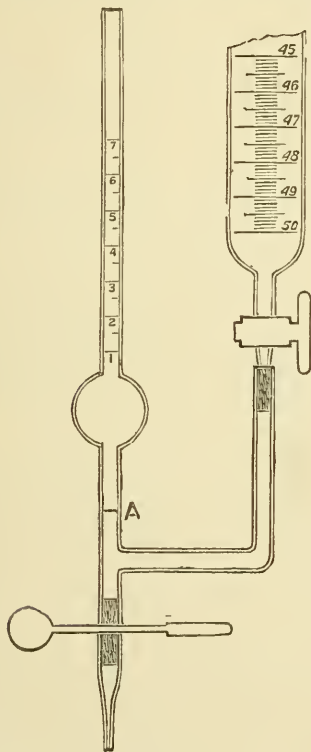


FIG. 2.

weighings of water. In order to avoid this standardisation the writer has used a pipette with a scale etched upon the stem as shown in the cut. It is only necessary to take care that when the pipette is filled to the mark etched at A that about 2 c.c. more will put the meniscus somewhere near the middle of the pipette scale. Starting with the burette filled to the zero reading and the lower meniscus coinciding with the mark at A, the first 2 c.c. of the burette scale are delivered into the pipette, and the pipette-scale reading noted. The pipette is then emptied to A, and the next 2 c.c. of the burette delivered. This operation is repeated down the length of the burette. One set of readings can be made starting from the zero point of the burette and another set starting from the 1 c.c. graduation mark. In order to apply the corrections it is only necessary to standardise the pipette scale against the burette scale by a few fractional fillings of the pipette. In applying the corrections any of the ordinary methods of calibration may be employed, such as assuming the first 2 c.c. of the

burette correct, and then distributing the deviations from the truth. For most laboratory work exceedingly small deviations are negligible, but the fact that a serious deviation from the truth may introduce a constant error into a series of observations, makes a rapid and easy method of becoming acquainted with the variations of burette scales of great value. This instrument permits this to be done with but little expenditure of time, and without the necessity of making a single weighing. Bad burettes can be immediately condemned, and those of sufficient accuracy for the work in hand selected. In case absolute corrections are demanded, the pipette can be standardised by the method of weighing much more easily than one that is not provided with an etched scale on the pipette stem. Of course the pipette must be made scrupulously clean with a chromic-sulphuric acid mixture before it is used.

A BIBLIOGRAPHY OF STEEL WORKS
ANALYSIS.

PART XI.

By HARRY BREARLEY.

(Continued from vol. lxxxiv., p. 250).

COPPER.

THIS section extends to the end of 1900. The items are arranged under the following heads:—

- I. SEPARATIONS FROM OTHER METALS.
- II. GRAVIMETRIC ESTIMATIONS.
- III. VOLUMETRIC ESTIMATIONS.
 - a. Cyanide Process.
 - b. Iodide Process.
 - c. Other Processes.
- IV. COLORIMETRIC ESTIMATION.
- V. DETECTION.
- VI. MISCELLANEOUS.

I. SEPARATIONS FROM OTHER METALS.

Iron (see also 1495, 1537, 1541, 1608).—

1472. LOEWE (C. N., i., 119).—After precipitating with AmHO, the $\text{Fe}_2(\text{HO})_6$ cannot be washed free from Cu; it must be dissolved and re-precipitated.
1473. GALETTI (C. N., xx., 248).—Precipitate iron with AmHO, add excess acetic acid, and again excess AmHO followed by acetic. This procedure prevents adhesion of Cu to precipitated iron. Cu titrated with ferrocyanide.
1774. MERRICK (C. N., xxvi., 115).—Decompose pyrites with HNO_3 , evaporate, and dissolve Cu from residue with dilute AmHO.
1475. BREARLEY (C. N., lxxviii., 14).—Iron can be precipitated from neutralised solutions as basic chromate perfectly free from copper, and Cu estimated as in 1569.
1476. FLAJOLO (C. N., ix., 193).—Precipitate Cu with hypo. The precipitate is free from Fe, Zn, Co, Ni, and P, but not As or Sb. Estimate Cu with KCN.
1477. CARNOT (C. N., liii., 172).—As 1476. Precipitated Cu_2S ignited with S in H and weighed.
1478. VORTMANN (Z. C. S., lxvi., ii., 35).—AmHO solutions of Cu electrolysed without filtering off precipitated Fe.
1479. FERNBERGER and SMITH (Z. S. C. I., 1900, 53).—Electro-separations of Fe, Cr, Zn, Ni, Co, Mn, &c., from Cu, using solutions of the phosphates in phosphoric acid.
1480. *Aluminium*.—HUNT, CLAPP, and HANDY (C. N., lxx., 225).—Cu precipitated with H_2S from acid solution of metallic Al, evaporated with HNO_3 , and weighed as CuO .

- Zinc** (see also 1479, 1518, 1524, 1541, 1543).—
1481. WITTSTEIN (C. N., xix., 156).—Zn dissolved from precipitated sulphides with dilute H_2SO_4 .
1482. BERGLUND (C. N., xlvii., 244).—Precipitate Cu with H_2S from definitely acidified solutions.
1483. KNORRE (C. N., lix., 222).—Precipitate Cu with nitroso- β -naphthol, and ignite to CuO (see 25 and 26).
1484. KAIKOW (Z. C. S., lxxviii., ii., 246).—Cu precipitated with hydrazine hydrochloride and KI (see 543 and 1543).
1485. SODERBAUM (Z. C. S., lxxii., ii., 348).—Cu is precipitated by a stream of acetylene quite free from zinc.
1486. MAWROW and MUTHMANN (Z. S. C. I., 1896, 381).—Cu is precipitated free from Zn and Cd, if no HCl is present, by adding hypophosphorous acid.
- Cadmium** (see 26, 1486, 1495, 1524, 1532, 1542).—
1487. BEHAL (C. N., li., 280) and WARREN (C. N., lxi., 125).—Add an alkaline solution of soda tartrate and boil. Cd is precipitated.
1488. GUCCI (C. N., li., 55).—Precipitate Cu with ammonium benzoate from acid solution.
1489. VORTMANN (C. N., xlv., 57).—Hypo. precipitates Cu free from Cd.
1490. HOFFMANN (C. N., ii., 159).—Cd is easily dissolved from mixed sulphides with H_2SO_4 .
1491. BROWNING (Z. C. S., lxxvi., ii., 68).—Cu precipitated as iodide, dried, and weighed; Cd in solution.
1492. BACKELANDT (Z. S. C. I., 1886, 510).—Cd is precipitated with KHO in the presence of glycerol. Cu is precipitated from the filtrate with glucose and weighed as CuO .
1493. WELLS (C. N., lxxiv., 294).—To neutral solution add hypo. until all colour goes; then precipitate Cd with Na_2CO_3 and filter off. On acidifying filtrate, Cu is precipitated.
1494. BORNEMANN (C. N., lxxxi., 53).—Cu precipitated from hot HNO_3 solutions with oxalic acid.
- Nickel** (see also 1479, 1537, 1541).—
1495. RUDORFF (Ag, Hg, Cd) (Z. C. S., lxxiv., ii., 305) and SMITH and MOYER (Cd, Zn, Co, Fe) (Z. C. S., lxxiv., ii., 496).—Electro-separations.
- Mercury** (see also 1584).—
1496. ROSENBLADT (Z. C. S., lii., 302).—Precipitated sulphides digested with K thiocarbonate. Hg and Pd dissolved.
1497. VON USLAR (C. N., lxxiii., 28).—Precipitate Hg as Hg_2Cl_2 with phosphorous acid from acidified solutions.
1498. JANNASCH (C. N., lxxiv., 145).—Hg volatilised from precipitated sulphides; or (Z. C. S., lxxvi., ii., 59), precipitated from $AmHO$ solutions with hydroxylamine.
1499. SMITH and MACAULEY (Z. C. S., lvi., 797; and lxxii., 239) and REVAY (Hg and As) (C. N., lxxix., 194).—Electro-separations.
- Lead** (see also 1525, 1584).—
1500. NISSENSON (Z. C. S., lxxvi., ii., 220) and CLASSEN (Z. C. S., liv., 529).—Electro-separations.
- Arsenic** (see also 1532, 1542, 1543, 1555, 1594).—
1501. PARNELL (C. N., xxi., 133).—Examines processes depending on solubility of As in Na_2S , passing chlorine through alkaline liquor containing precipitated sulphides, and heating in Cl gas and H.
1501a. CLASSEN (Z. C. S., liv., 528).—By volatilising As from HCl solution.
1502. JANNASCH (Sb and Sn) (Z. C. S., lxxviii., ii., 89 and 462).—By volatilising in a stream of HCl gas.
1503. GUCCI (Z. C. S., liv., 630).—Cu precipitated with KHO .
1504. MCKAY (Z. S. C. I., 1890, 822), SMITH and FRANKEL (Z. S. C. I., 1890, 1067), and SCHMUCKER (Z. S. C. I., 1894, 280).—Electrolytic.
- Antimony** (see also 1502, 1549, and 1555).—
1505. LUCAS (C. N., lxxix., 78).—Treat mixed sulphides with Na_2S , destroy polysulphides with H_2O_2 , and electro-deposit Sb without removing CuS , as in 516.
1506. FINKENER (Z. S. C. I., 1889, 733).—Add alkaline fluoride, and then KI and SO_2 . The filtrate contains Sb_2O_3 and a little Cu, which are separated with H_2S and Am_2S .
1507. SMITH and WALLACE (Z. S. C. I., 1893, 1063).—Electro-separation.
- Bismuth**.—
1508. LOWE (C. N., xlviii., 296).—Precipitate with $NaHO$, re-dissolve in glycerin, and precipitate Cu with glucose in the cold. Bi in solution.
1509. JANNASCH (Z. C. S., lxxvi., ii., 71).—Bi precipitated with $AmHO$ and H_2O_2 .
1510. SMITH and SALTAR (Z. S. C. I., 1893, 605).—Electro-separation from a citrate solution containing regulated amount of KCN.
- Silver** (see also 1495, 1584).—
1511. REVAY (Z. S. C. I., 1898, 184) and KUSTER and STEINWEHR (Z. S. C. I., 1898, 466).—Electro-separations.
- Selenium**.—
1512. VIOLETTE (C. N., xxi., 178).—Heat strongly in current of dry air; the Se is sublimed as a white crystalline ring.
- Palladium** (see also 1496).—
1513. WÖHLER (C. N., xv., 40).—Cu precipitated with SO_2 and KCNS.
- Thallium**.—
1514. CROOKES (C. N., vii., 133 and 218).—Precipitate Tl as sulphide from alkaline cyanide solution; or, precipitate metals as subiodides and dissolve out the Cu with $AmHO$. Metallic Cu frequently contains Tl.
- II. GRAVIMETRIC ESTIMATIONS.
1515. STORER (C. N., iii., 70).—Deposit Cu from H_2SO_4 solutions with iron, and heat in nitrogen before weighing to destroy organic matter.
1516. KERN (C. N., xxxi., 76).—Cu-Sn-Zn alloys, after decomposition, are precipitated as metals on Fe, Zn, &c.
1517. VILLIERS (C. N., lxxviii., 263).—Precipitate Cu with Mg, wash with alcohol, dry at $100^\circ C$, and weigh. An alloy is precipitated if Zn is present.
1518. WARREN (C. N., lxi., 136; and lxxi., 92).—Decompose Zn-Cu alloy with strong H_2SO_4 , precipitate Cu with Mg, and weigh. After adding soda acetate, Zn may be precipitated similarly.
1519. SHENGLE and SMITH (C. N., lxxxi., 134).—Cu precipitated by zinc always contains more or less of the latter metal.
1520. MOHR (C. N., vi., 229).—Decompose ore with H_2SO_4 , evaporate, and boil dry residue with water. Cu and a little Fe dissolve; precipitate Cu with Zn and wash out of contact with air.
1521. SUTTON (C. N., vi., 275).—A score of common elements have no influence on 1520.*
1522. LOWE (C. N., ii., 191).—Cu is completely precipitated by a slight excess of oxalic acid.
1523. GIBBS (C. N., xvii., 172).—Cu is completely precipitated by boiling with small excess of Na_2CO_3 . The metal reduced in H is free from alkalis (see also FIELD, C. N., ii., 279).
1524. WARREN (C. N., lxxiii., 193).—Precipitate with glucose from solution containing $NaHO$ and Rochelle salt and weigh as CuO . Zn and Cd perfectly separated. For various means of esti-

* Simple replacement of copper by either Zn, Mg, or Fe is found in no case to be exactly true. Clowes's paper (C. N., lxxviii., 155) may be taken as a type of many others.

- matting the suboxide precipitated by glucose, see C. N., xlv., 262.
1525. JANNASCH and LEZCINSKY (C. N., lxix., 7).—Separate Pb from AmHO solution with H_2O_2 . Precipitate Cu in H_2S and heat in air which has passed through Am_2CO_3 , so as to decompose any CuSO_4 formed.
1526. MILLON and COMMALE (C. N., viii., 100).—Copper always escapes with the nitrous vapours on heating $\text{Cu}(\text{NO}_3)_2$. Weigh as Cu after reducing in H.
1527. WEGSCHEIDER (J. C. S., lxvi., ii., 31).—Particulars of temperature and nature of atmosphere to be attained when Cu is estimated as cuprous sulphide (see also 1578).
1528. DEBRAY and JOANNIS (C. N., l., 234 and 248).—A temperature high enough to melt or even frit CuO partly decomposes it.
1529. ULRICI (C. N., xx., 118).—Ignited precipitate formed with H_2S is weighed as though Cu_2S , but really it is always a mixture of CuO and Cu_2S .
1530. HOLTHOF (C. N., lxi., 193).—Precipitated sulphide ignited while moist passes to oxide completely. Dried precipitates contain SO_3 after ignition.
1531. STICKNEY (J. C. S., lxx., ii., 523).— Cu_2S is reduced to copper when heated in contact with a Bunsen flame.
1532. NISSENSON and NEUMANN (J. C. S., lxx., ii., 450).—Cu precipitated with hypo. is oxidised completely to CuO in the muffle. Any As is expelled. Cd does not interfere. Also WILLENS (J. C. S., lxxviii., ii., 315).
1533. TROILIUS (J. I. S. I., 1883, 367 and 710).—Precipitate H_2SO_4 solution of steel with hypo.; re-dissolve and re-precipitate, and ignite moist precipitate to CuO.
1534. REINHARDT (J. I. S. I., 1889, ii. 481).—Reduce ferric solution with hypophosphite and precipitate Cu with H_2S . H_2SO_4 (3:1) dissolves basic pig without attacking contained copper.
1535. ZIEGLER (J. S. C. I., 1893, 377).—Ammonium sulphocarbonate, which is more agreeable in use than H_2S , precipitates Cu from FeO solutions of steel.
1536. REIS (J. I. S. I., 1891, i., 441).—HCl solution of steel is treated with H_2O_2 to bring any undissolved Cu into solution; then reduced as 1534, and Cu precipitated with sulphocarbonate and ignited to oxide.
1537. KLEIN (J. S. C. I., 1887, 836).—Add ammonium dithiocarbamate to hot HCl solution. Ignite precipitate with S in H and weigh as Cu_2S . Fe, Mn, and Ni do not interfere.
1538. PARRY and MORGAN (C. N., lxvii., 259).—Precipitate from FeO solution with H_2S or hypo., and re-precipitate with NaHO or ignite at once to CuO. Also, digest nearly dried residue of 20 to 50 grms. of steel with AmHO and compare blue colour with standards.
1539. NAHUSEN (C. N., lx., 133).—Decompose pyrites with $\text{H}_2\text{SO}_4 + \text{HNO}_3$, precipitate with H_2S , dissolve out As and Sb with Na_2S , and estimate Cu as sulphide.
1540. BLOXAM (C. N., xi., 196).—On digesting the sulphide with Am_2S , a portion of the Cu dissolves as $\text{Cu}_2(\text{NH}_4)_2\text{S}_7$.
1541. GIBBS (C. N., xvii., 160).—Precipitate from H_2SO_4 solution with Mg hypophosphite, ignite in H, and weigh as Cu. Fe, Mn, Ni, and Zn do not interfere; Sb, As, HCl, and HNO_3 do.
1542. SODERBAUM (J. S. C. I., 1897, 563).—Cu precipitated from alkaline solution with acetylene. Dissolve acetylide in HNO_3 , filter from C, evaporate, and ignite to CuO. J. C. S., lxxiv., ii., 191.—As and Cd are separated from Cu in this way.
1543. JANNASCH and BIEDERMANN (C. N., lxxxii., 282).—Hydrazine sulphate precipitates metallic Cu from NaHO solutions free from Zn, As, and nearly Sn. Cu weighed as CuO.
1544. TAMM (C. N., xxiv., 91).—Precipitate as sulphocyanide (see 1584), digest with Am_2S , and weigh as Cu_2S . Cu may be separated as CuCNS from all other elements.
1545. MILLON and COMMALE (C. N., vii., 218).—Process for estimating Cu (or Ag) or mixtures of CuO and Cu_2O is based on the fact that AmHO solutions of Cu_2O precipitate Ag from silver solutions.
1546. GIBBS (C. N., xi., 173).—Precipitation with Zn accurate (see 1519). Suggests electro-deposition from sulphate solutions.
1547. LUCKOW (C. N., xix., 221).—Dissolve roasted ore in acid and electro-deposit Cu. Behaviour of associated elements.
1548. HAMPE (C. N., lxvii., 103).—Small quantities of Sb are always electro-deposited with Cu. So also is Bi (C. N., lxviii., 51). The Bi may be removed as oxychloride (STAHL, J. C. S., lii., 529). See also SMITH and SALTAR (J. C. S., lxiv., ii., 495), who say Pb is also deposited.
1549. SMITH and WALLACE (J. C. S., lxiv., ii., 495).—No Sb is deposited with the Cu from AmHO tartaric solutions.
1550. CHASSY (C. N., lxx., 97).—On electrolysis a heated CuSO_4 solution deposits Cu_2O .
1551. MERRICK (C. N., xxxiii., 111).—Can determine 0.0001 grm. Cu by depositing on Pt.
1552. MACKINTOSH (C. N., xlv., 279; and xlv., 101).—Deposition from nitro-citric acid solutions too high; from HNO_3 alone difficult to precipitate all the Cu. CuSO_4 solutions best.
1553. RUDORFF (J. C. S., lxiv., ii., 93).—From faintly HNO_3 —or, if Cl is present, from AmHO—solutions. Soda acetate is added before stopping the current.
1554. DROSSBACH (J. C. S., lxiv., ii., 93).—Electrolyse AmHO solutions only until the Cu is precipitated. Hg, Cd, Pb, and Ag are the only interfering elements.
1555. CETTEL (J. C. S., lxviii., ii., 139).—Best deposited from AmHO solution if Cl, As, or Sb are present. Pb, Bi, Hg, Cd, and Ni interfere.
1556. CLASSEN (J. C. S., lxviii., 1095; and lvi., 77) and WAGNER (J. C. S., lxxii., ii., 520).—Deposit from oxalate solutions at 70–80° C.
1557. HOLLARD (C. N., lxxvii., 31).—Electrolytic methods for complete analysis of brass and bronze.
1558. BRAND (J. S. C. I., 1889, 1011).—From pyrophosphate solutions.
1559. WOLMAN (J. C. S., lxxiv., ii., 50).—Best results obtained by deposition from H_2SO_4 or HNO_3 solutions.
1560. MOORE (C. N., liii., 209).—Deposits from alkaline KCN solutions at 70°.

(To be continued.)

Examinations in Modern Languages.—The Society of Arts is endeavouring to extend its modern languages examinations, so as to make them include a *viva voce* test. The written examinations are now carried on at 300 centres throughout the United Kingdom. A notice has been sent out to all these centres, to the effect that a *viva voce* examination will be held at any centre where 24 candidates can be collected, at a fee of 2s. 6d. a head. The Society's examinations include all modern languages of commercial importance, but at present *viva voce* examinations will only be held in French, German, and Spanish. The tests are to include dictation, reading, and conversation.

EXPERIMENTS RELATIVE TO THE CONSTITUTION OF PECTOLITE, PYROPHYLLITE, CALAMINE, AND ANALCITE.*

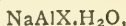
By F. W. CLARKE and GEORGE STEIGER.

(Concluded from p. 66).

Analcite (continued).

IN order to discuss the constitution of analcite, let us recur to the analysis of the mineral itself. It is at once evident from the comparison made on a preceding page that our sample of the mineral varies notably in composition from the requirements of theory. The silica is 2.5 per cent too high, while alumina and soda are correspondingly low. No probable impurity and no presumable errors of manipulation can account for so great a divergence. If we consult other analyses, as we find them tabulated in manuals like those of Dana and of Hintze, we shall find other cases resembling this, and also examples of variation in the opposite direction, with silica low, and an apparent excess of bases. Most analcite gives quite sharply the metasilicate ratios required by the accepted formula; but the variations from it are large enough, common enough, and regular enough to command attention. The analyses are not all covered by the recognised theory, and the apparent irregularities are not fortuitous, but are systematic in character.

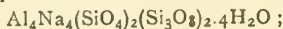
One explanation of the seeming anomalies is simple and clear. If analcite, instead of being a metasilicate, is really a mixture of ortho- and tri-silicate, then all of the analyses become intelligible. In most cases the two salts are commingled in the normal ratio of one to one; but in our analcite the trisilicate predominates, while in some other samples the ortho-salt is in excess. All reduce alike to the simple expression—



in which X represents $n\text{SiO}_4 + m\text{Si}_3\text{O}_8$; a formula which agrees with evidence from various other sources.

For example, analcite may be derived in nature either from albite, $\text{AlNaSi}_3\text{O}_8$, or nephelite, AlNaSiO_4 , and, on the other hand, alterations of it into feldspars have been observed. Its closest analogue, leucite, has yielded pseudomorphs of orthoclase and elæolite; while leucite and analcite are mutually convertible each into the other. The evidence of this character, the evidence of relationship between analcite and other species, is varied and abundant, and the simplest conclusion to be drawn from it is that which has been given. Every alteration, every derivative, every variation in the composition of analcite points to the same belief. The consistency of the data can not well be denied.

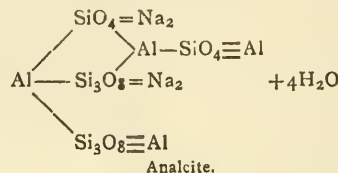
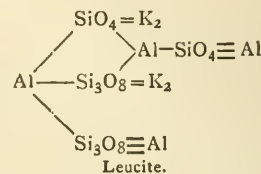
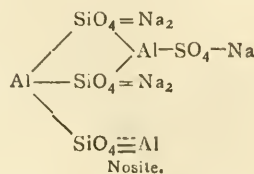
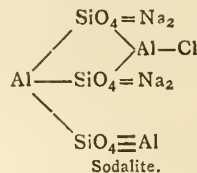
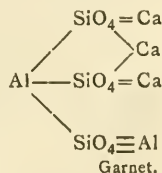
In the case of a normal analcite—that is, one which conforms to the usual empirical formula—the expression which best represents these relations is—



and this accords with the minimum molecular weight as determined by the study of our ammoniated residue. Structurally, this is comparable with the formulæ of garnet, zunyite, sodalite, nosite, and leucite; all of which are also isometric in crystallisation. The more important of the symbols are given in next column.

That is, analcite and leucite become members of the garnet-sodalite group of minerals, and their relations to nephelite, albite, prehnite, natrolite, &c., natural and artificial, are perfectly clear. In analcite there may be admixtures of strictly analogous ortho- or tri-silicate molecules; but these remain to be separately discovered.

Now, these formulæ are not ultimate verities to be blindly accepted. They are simply expressions which represent composition, and a wide range of established relationships, and which serve a distinct purpose in the correlation of our knowledge. Properly used, with due



recognition of their limitations, they are helpful, and suggest possibilities of research; misused, they may become mischievous. They now satisfy all known conditions, and that is a sufficient warrant for their existence.

ON PYRITE AND MARCASITE.*

By H. N. STOKES.

(Continued from p. 65).

IV. DATA FOR PYRITE.

THE following table gives duplicate determinations of ρ , made upon well-crystallised samples of pyrite free from visible impurities, but otherwise selected at random:—

Determinations of ρ made upon Samples of Pyrite.

No.	Locality.	Density.	ρ .	Mean value of ρ .
1.	Unknown	—	$\left. \begin{array}{l} 60.1 \\ 59.9 \end{array} \right\}$	60.0
2.	Custer County, Colo. ..	5.018	$\left. \begin{array}{l} 60.4 \\ 59.7 \end{array} \right\}$	60.0
3.	Roxbury, Conn.	5.023	$\left. \begin{array}{l} 61.2 \\ 60.9 \end{array} \right\}$	61.0
4.	Leadville, Colo.	—	$\left. \begin{array}{l} 60.2 \\ 60.2 \\ 60.4 \end{array} \right\}$	60.3
5.	Old Jordan mine, Utah..	5.041	$\left. \begin{array}{l} 60.5 \\ 61.1 \end{array} \right\}$	60.8
Mean value of ρ 60.4.				

- No. 1. A large cube, with slight tarnish and splendid conchoidal fracture. Traces of silica, copper, and arsenic.
- No. 2. Octahedron, with fracture on peripheral part conchoidal, on the interior somewhat uneven or granular. Slight trace of copper.
- No. 3. Combination of cube and octahedron, with conchoidal fracture. Traces of copper and arsenic.
- No. 4. Cubes. Traces of silica and copper.
- No. 5. Cubes, splendid conchoidal fracture. Trace of copper.

* Bulletin of the United States Geological Survey, No. 167.

* From the Bulletin of the U.S. Geological Survey, No. 186.

Oxidation Coefficient of Pyrite.

From the above figures it appears that the oxidation coefficient of pyrite is not likely to vary more than 0.6 per cent on duplicate determinations, and that it may vary about 1 per cent in typical specimens, which do not contain more than traces of impurities that can influence the result. Whether this difference is due to the chemical action of the impurity on the solvent, to its electrochemical action on the pyrite, or to slight physical differences in the pyrite itself, can not be decided at present. The oxidation coefficient of pure pyrite may be assumed to be 60.4. Figures higher than 61 or lower than 60 may be taken to indicate greater contaminations, which can usually be detected by analysis, and the influence of some of which it is pointed out below.

V. DATA FOR MARCASITE.

The following table gives the values of p (mostly in duplicate) for various samples of marcasite, which were selected as being free from visible impurity and showing characteristic crystallisation. Other specimens, which were found to contain pyrite, are described in a later section.

Values of p for Various Samples of Marcasite.

No.	Locality.	Density.	p .	Mean value of p .
6.	Dover Cliffs, England ..	4.881	16.3	16.3
7.	Galena, Ill.	4.891	16.9 16.1	16.5
8.	Galena, Ill.	—	16.5 26.7	16.6
9.	Linden mine, Wis. . .	4.901	16.3 16.9	16.6
10.	Galena, Ill.	4.886	17.4 17.3	17.4
11.	Hazel Green, Wis. . .	4.896	18.1 17.5	17.8
12.	Weardale, England . .	4.880	18.0 18.0	18.0
13.	Cornwall, England . .	4.878	18.7 18.3	18.5
14.	Webb City, Mo. . . .	4.887	18.6 18.8	18.7

No. 6. This is the specimen described by Julien (*Annals New York Acad. Sci.*, 1887, vol. iv., p. 172) as follows:—"No. 14, Marcasite, Dover Cliffs, England. A brilliant cluster of spearheaded crystals—broad, striated, twinned plates—embedded in light grey chalk, greyish white, and brilliant on fracture." Some of the crystals carry small pyrite crystals along the plane of twinning, which are visible only after cleaning with acid. Only those free from visible pyrite were used for the determination.

No. 7. A hollow stalactite from Galena, Ill. The inner portion is fibrous, the outer columnar, with pyramidal terminations. Tarnish, copper coloured. Colour of fresh fracture or clean surface, tin-white. It contains a trace of copper, and is free from arsenic. Only the outer columnar portion was used.

No. 8. A similar stalactite from Galena, Ill., with greenish-grey tarnish on fracture, and bronze-coloured on surface, and with decided vitriolisation.

No. 9. Curved wedge-shaped crystals of the Joplin type, from Linden mine, Wisconsin. Iridescent blue and yellow tarnish. Fracture, tin-white. The specimen carried a little galena and calcite, from which it was carefully freed by acid and by picking out. Analysis showed a trace of copper and a little lead.

No. 10. Galena, Ill. A compact mass of large acute pyramidal crystals branching out from a common

axis. Tarnish, greenish-yellow. Colour on fresh fracture and on green surface, tin-white. A few crystals of chalcopryrite. Material carefully selected for determination gave traces of silica and copper, and no arsenic.

No. 11. Hazel Green, Wis. A thick crust on calcite, with distinct rhombic crystallisation. Colour, tin-white. Contains traces of lead and copper, and is free from arsenic.

No. 12. Weardale, England. Flat, deeply striated crystals, with slight bluish tarnish. Colour of clean surface, tin-white. No visible impurity was observed, and analysis showed the presence of a faint trace of copper and a little silica, and the absence of arsenic.

No. 13. Cornwall, England. Flat crystals, with slight bluish tarnish. Colour of cleaned surface, tin-white. A few of the crystals carry minute cubes of pyrite, and such were rejected. Analysis showed no arsenic, and a trace of copper and antimony. The high oxidation coefficient makes it possible that it encloses considerable pyrite, but material was wanting for a special determination of this.

No. 14. Webb City, Mo. Curved wedged-shaped crystals of the Joplin type, on sphalerite and calcite, and with a little enclosed chalcopryrite. Analysis of a sample used for the determination showed some lead and copper, which probably account for the high figure obtained.

Oxidation Coefficient of Marcasite.

From the above figures it appears that specimens of apparently pure marcasite differ somewhat more with regard to the oxidation coefficient than does pyrite. It will appear below that an admixture of small quantities of pyrite lowers the value of p , notwithstanding the fact that pyrite has a higher oxidation coefficient. It is probable that other sulphides in minute amount exert a similar effect to even a greater extent, possibly in part because of the electrochemical action which they produce. The marcasite with the lowest oxidation number is therefore not the purest. The specimen No. 12 from Weardale was the purest examined, and I incline, therefore, to adopt the figure 18 as being nearest to the oxidation coefficient of pure marcasite. Figures higher than this, as well as lower than 16.5, must be regarded as indicating contamination, either with pyrite or with another oxidisable mineral. It also appears from the examination of certain samples (Nos. 22 and 23) that marcasite may carry considerable amounts of pyrite so intimately intergrown as not to be visible upon examination of small fragments under a lens after cleaning with acid.

VI. MIXTURES OF PYRITE AND MARCASITE.

It is desirable to construct a curve which shall give the oxidation coefficients of mixtures of pyrite and marcasite. Such a curve would enable us to ascertain, in the absence of other indications, whether a given specimen contains one or the other or both of these minerals, and in the latter case to determine their relative amounts. It would enable us to test the hypothesis of Julien (*Annals New York Acad. Sci.*, 1887, vol. iv., p. 213), whose statement I quote:—

"The forms of iron pyrites occurring in nature are intimate mixtures of these three minerals; rarely of pyrrhotite, however, on account of its ready metasomatic alteration into one or the other of the triad. These common mixtures of marcasite and pyrite may originate by inclosure during crystallisation, by alteration, and by displacement, and pass progressively into complete paramorphs, well crystallised after the form of one or the other mineral.

"The latent constitution of these composite minerals is

indicated by variation in density, exactly proportionate in most cases to the amount of each constituent (compare table on p. 33), and by a similar variation in other physical properties; e.g., hardness, fracture, resistance to decomposition, and even in colour, in the case of the paramorphs of marcasitic pyrite."

As a paramorph consists simply of minute crystals of the one substance massed together in a form which characterises the other, it is obvious that the oxidation coefficient must correspond to that substance of which the specimen really consists, not to that which it imitates, and such a curve would indicate the proportions in the case of a mixed crystal. It would further enable us to follow the possible artificial transformation of one into the other, and would serve as an aid in synthetic work. In such work it is frequently difficult to obtain products sufficiently well characterised to admit of positive identification in the absence of optical properties and well developed crystallisation. Such a curve would render us independent of these.

It is not possible to calculate the curve for mixtures of pyrite and marcasite from the oxidation coefficients of the two minerals. The oxidation coefficient is influenced by the concentration of the ferric and ferrous salts and the sulphuric acid. With the pure mineral these vary in a perfectly constant manner in the case of each sulphide, but when each mineral is decomposing in the presence of the products formed by the other, nothing short of an elaborate investigation could give us the data for calculating the effect in any case. It is therefore necessary to construct the curve empirically, from data obtained from a sufficient number of artificial mixtures.

Conditions under which the Oxidation Coefficients of Mixtures may be Determined.

We have seen that the oxidation coefficients of pyrite and marcasite are independent of the relative amounts of solvent and solute, and of the degree of comminution, and are constant for a given temperature and concentration provided the reduction be complete. The case of a mixture of the two is more complicated. Here each component deprives the other of a portion of the ferric salt, this effect being greater the greater the surface, or, what is the same, the finer the powder. An artificial mixture of given composition will therefore show a varying oxidation coefficient depending on the relative degree of fineness of the two components. Moreover, since a given volume of the standard ferric solution decomposes about 2.26 times as much marcasite as pyrite, the ratio between the surfaces is constantly changing, and it is no longer a matter of indifference whether a large or a small amount of material be acted on by a given volume of solution.

If, however, the minerals be ground together, and if the grinding be tolerably thorough, then, considering their approximately equal hardness, it may be assumed that the ratio of the surfaces for a given mixture will remain practically constant, and if the value of p be obtained by using such an excess of the mixture that this ratio is not appreciably altered during the experiment, or if the same amount of mixture and of solution be used in every case, it becomes possible to obtain concordant values of p and to construct the desired curve. The assumption that the ratio of surfaces remains constant during grinding is not absolutely true, but practically it is, as the duplicate results presented below were each obtained from different samples, so that the slightly varying hardness of different specimens and the different degree of fineness to which they are ground introduce no greater errors than those which are inherent in the method itself. In each case the materials were broken up so as to pass a 20-mesh but to be retained by a 60-mesh sieve, were carefully weighed, mixed, and ground so as to avoid all loss, and 1 to 1.02 grms. of the mixture and 250 c.m.³ of the solution were used in each experiment.

(To be continued),

NOTICES OF BOOKS.

The Carbides of Hydrogen ("Les Carbures d'Hydrogène"), 1851-1901. Experimental Researches. By M. BERTHELOT, Sénateur. Three volumes. Paris: Gautier-Villars. 1901. Pp. 1431.

THE work now presented to the chemical world contains the results of the author's researches on the carbides of hydrogen, and principally on their synthesis from their elements, which synthesis is the pivot on which all other syntheses in organic chemistry turn.

The formation of acetylene, of ethylene, of formene, and of benzene, the four fundamental carbides, that of the pyrogenic carbides, and the general methods for the hydrogenation of the carbides and other organic compounds, have been the constant study of the author for half a century, his first work in this direction being undertaken in the year 1851, and the last being completed in 1901.

This great work is divided into three volumes; Volume I. is on "Acetylene; the Complete Synthesis of Carbides of Hydrogen," and comprises two books. In Book I. the author fully describes the synthesis of acetylene, formene, ethylene, benzene, and the polymeric carbides of acetylene. Book II. is devoted to the derivatives of acetylene; that is to say, the compounds resulting from its union with elements, such as nitrogen, hydrogen, oxygen, the halogens, and metals.

In the second volume M. Berthelot describes his experiments with the pyrogenic and some other carbides belonging to the propylic acid camphenic series. This volume is also divided into two books. Book III. deals with the pyrogenic carbides derived from acetylene and from the most simple carbides, submitted to the action of high temperatures. He also examines the action of heat on the mixed carbides, and the thermo-chemical relations between these different carbides. Book IV. is on propylene, its isomer trimethylene, and the allylic series, as well as the terebenthenic, camphenic, and terpilenic carbides.

In volume three the author gives his experiments on the general formation of the derivatives of the carbides of hydrogen. This volume is divided into three books. Book V. deals with the hydrogenation of the carbides and organic compounds generally; this hydrogenation is effected by a method of universal application founded on the use of hydriodic acid, a method discovered by the author in the year 1857, and further developed in 1863. Book VI. treats of the oxidation of the carbides of hydrogen and their transformation into aldehydes and acids by various methods.

Finally, in Book VII. we have the synthesis of the alcohols by means of the carbides of hydrogen, either by hydration or by oxidation; a general and direct method is also described, destined to establish the alcoholic function of various principles, such as Borneo camphor and cholesterine, which had not yet been regarded as alcohols.

These three volumes, which represent a scientific lifetime, are of the greatest value not only to specialists, but to those whose tastes incline them to keep up with the march of scientific knowledge and the discovery of truth, and will remain a monument to the greatness and fame of its author.

Beiträge zur Chemischen Physiologie und Pathologie. Edited by FRANZ HOFMEISTER. Band I., 7-9 Heft. Braunschweig: Friedrich Viewig und Sohn. 1901.

THE December number of these "Beiträge" includes amongst others a paper on the mutual action of the enzymes upon one another, by A. Wroblewski and two collaborators, in which is established experimentally the general conclusion that this action is very limited, as proved in the cases of pepsin, trypsin, diastase, and invertin; also an exhaustive report of investigations as to

the seat of the synthesis of sulphuric acid ethers in the animal body, which Drs. Embden and Glaessner believe they have proved to be principally the liver. Of more purely chemical interest are two shorter papers on the Aromatic Groups in the Albumen Molecule and Glue respectively.

Elektrische Verbrauchsmesser der Neuzeit. By JOHANNES ZACHARIUS. Halle-a-S.: Wilhelm Knapp. 1901.

ACCORDING to the author of this book, the theory of the construction of the electricity meter has received but little attention in recent years, and the paucity of literature on the question has led him to make this attempt to bring together all that is at present known of the subject. The book commences with an historical account of the development of such apparatus, and includes sections on the standardisation, reading, and choice of a meter. A considerable part of the book is devoted to a list of patents of electricity meters and allied apparatus from the year 1881 to 1900 inclusive, together with short abstracts of the specifications. The diagrams and illustrations throughout the book are particularly plentiful and good.

Die Pflanzen-Alkaloide. By JUL. WILH. BRÜHL, EDVARD HJELT, and OSSIAN ASCHAN. Braunschweig: Friedrich Vieweg und Sohn.

THIS monograph on plant alkaloids forms a part of the eighth volume of the revised edition of Roscoe and Schorlemmer's "Complete Text-book of Chemistry," and deals with all known plant alkaloids and bases related to them. It is not too much to say that it is probably the most complete book on the subject extant, and will no doubt appeal to a wide circle of scientific readers. The subject is treated chiefly from an historical point of view, and the accounts of classical work on the constitution of many of the substances are most interesting and stimulating.

The authors display a perfectly unbiassed spirit in putting before their readers views which may still be regarded as disputed; as, for example, in the case of Merling's and Willstätter's excellent work on the constitutional formula of tropine. As far as possible, the alkaloids are grouped together as derivatives of pyrrolidine, pyridine, quinoline, and isoquinoline, but a large number which cannot be identified as derivatives of any of these bases are classed as "alkaloids of unknown constitution." Under this heading are included only those whose empirical formulæ are fairly well established; they are arranged according to the botanical families of the plants from which they are obtained. An appendix on gluco-alkaloids, and some alkaloids, such as artarine and fumarine, which appear to stand alone, is added. Such a work as this cannot fail to have a favourable reception, and the hope of the authors expressed in the preface, that the biologist, physician and pharmacologist, as well as the chemist, may find it useful and instructive, will without doubt be fulfilled.

Remarks on Molybdenum Oxides.—Marcel Guichard.—The author refers to the work of M. Klason and M. Bailhache on the subject of the blue oxides of molybdenum. His own researches lead him to the conclusion that the plurality of the blue oxides has not been demonstrated. The constitution of these bodies is perfectly unknown, several different formulæ being possible to represent each. It seems natural to attribute, to the blue oxide, a formula containing a molybdyle or a molybdenyl group, on account of such a formula corresponding to about 68 per cent of the metal. The author now suggests a formula containing molybdic acid and molybdenum oxide, because the compound behaves under all circumstances during its reactions as a molybdate of molybdenum oxide.—*Comptes Rendus*, cxxxiv., No. 3.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 3, January 20, 1902.

Properties of Lime at its Fusing-point.—Henri Moissan.—When graphite is placed in contact with lime at its fusing-point it becomes surrounded with a layer of calcium carbide, $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$. If the melted lime is in excess and the action is prolonged the carbide becomes oxidised and calcium liberated— $\text{CaC}_2 + 2\text{CaO} = 3\text{Ca} + 2\text{CO}$. If silicon is treated in a similar manner it at once becomes transformed into silica, and this forms a basic silicate in presence of excess of lime. In the case of boron, borate of calcium is formed; but if the experiment is of very short duration the residual boron becomes surrounded with little black crystals of calcium boride, CaB_6 . A number of metals when treated in this way, particularly when oxidation does not take place, are easily obtained in a crystalline state by simple vaporisation in a bath of melted lime. At this high temperature boiling platinum unites with calcium. Percentages of from 2.54 to 3.01 of lime have been found in the non-volatilised metal.

Critical Constants and Molecular Complexity of Certain Organic Compounds.—Ph. A. Guye and Ed. Mallet.—The authors make a series of measurements on the critical constants of anisol, phenetol, *m*-cresol, aniline, dimethyl-aniline, and dimethyl-*o*-toluidine, and from the numbers obtained they conclude (1) that the capillary ascensions of aniline indicate a slight polymerisation in the liquid phase, at low temperatures (considerably under boiling-point); (2) the capillary ascensions of meta-cresol show that at temperatures near its boiling-point this compound is still partially polymerised in the liquid phase. The authors extend their research to the case of the nitriles, and find that the numbers obtained confirm and generalise MM. Dutoit and Friderich's conclusion.

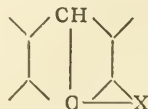
Certain Physical Properties of Selenium Hydride.—MM. de Forcrand and Fonze-Diacon.—The authors determine the temperature of liquefaction and ebullition of selenium hydride, under atmospheric pressure; also its density in the liquid state at its boiling-point, the temperature of solidification, and its solubility in water; all experiments have to be effected as rapidly as possible, to avoid the spontaneous alteration of this gas in presence of mercury and under the influence of light. However, this decomposition is slower than up to the present time was believed; in darkness it is almost nothing at the end of two or three days, and the authors found only 15 per cent of free hydrogen in a specimen of pure selenium hydride, after a week of exposure to full daylight, in presence of mercury.

Decomposition of Acetylene during Combustion.—Fernand Gaud.—The author's experiments were at first performed on burning jets of chemically pure acetylene, then on jets of gas to which each of the ordinary chemical impurities was methodically added, and he shows that under certain circumstances the heat evolved by the substance of the jet can be transmitted to the gas and favours the decomposition into its elements, and it is certain that the presence of sulphuretted hydrogen, and of the thionic products, is sufficient to provoke this decomposition during the formation of the flame:

Action of Mono-halogenated Propionic Ethers on Sodium Acetylacetone.—Fr. March.—Resuming his research on the action of the halogenated ethers of saturated acids of the fatty series on sodium acetylacetone, the author causes α -bromopropionate and β -chloropropionate of ethyl to react on this sodium salt. These

two reactions enable him to prepare α -methyl- β -diacetylpropionate of ethyl and β -diacetylbutyrate of ethyl.

Tribromo- and Triiodo-dinaphthoxanthonium; also the Bibromated Hydrobromic Ethers and Biodated Hydriodic Ethers of the supposed Binaphthylene-glycol.—R. Fosse.—In a preceding paper the author attributed the constitutional formula—



to the mono-halogenated derivatives to the xanthenes, obtained either by the action of the hydracids on the oxydols, or by the action of the halogens on the xanthenes. The bodies represented by this formula, where the oxygen behaves as a tetrad, by uniting one liaison to the opposed carbon group, ought to be able to fix two atoms of a halogen giving tri-halogenated derivatives. Experiment verifies this hypothesis.

Chemical Modifications taking place in a Plant subjected to the Influence of Sodium Chloride.—E. Charabot and A. Hébert.—The authors' investigations lead them to the conclusions that the addition of sodium chloride to the soil in which a particular plant is growing causes (1) an increase in the percentage proportion of organic matter in the plant; (2) a relative loss of water. At the same time that it exerts this double influence on vegetable life, sodium chloride favours etherification, and retards the transformation of menthol into methone.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Lord Iveagh, William Asch, Esq., Rev. S. J. Norman, Hunter Finlay Tod, Esq., James Martin White, Esq., George Westinghouse, and Lieut.-Col. Richard de Villamil were elected Members. The thanks of the Members were returned to Sir Frederick Bramwell, Bart., F.R.S., for his donation of £100, and to Mr. Frank McClean, F.R.S., for his donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures. It was announced that the following valuable relics of Michael Faraday, bequeathed to the Royal Institution of Great Britain by the late Mr. Thomas J. F. Deacon, of Newcastle-on-Tyne, had been received:—Medals of Silver and Bronze (numbering twenty in all), and including the Fuller Medal of 1828, two Copley Medals of 1832 and 1838, two Newton Medals of the Royal Society, 1833 and 1838, and the Rumford Medal of 1846; and two Foreign Orders contained in a small mahogany box. A Book of Portraits and Autographs, including original letters from the Prince of Wales and Prince Alfred (written in 1856), Louis Napoleon, Emperor of France, Humphry Davy, Thomas Young, Humboldt, John Dalton, Whewell, Mary Somerville, and many others. A Daguerrotype of a consultation of Faraday with Professor Daniell; a Drawing in colours of the Laboratory of the Royal Institution, by a niece of Sir John Moore; and a Manuscript Book entitled "A Class Book for the Reception of Mental Exercises, instituted July, 1818," containing contributions by Faraday. The late Mr. Deacon requested that the Medals and Orders should be preserved with an inscription showing that Margery Ann Reid and Caroline Deacon (*née* Reid), nieces of Faraday's wife, often lived with Faraday and his wife during the most brilliant period of his life, and are mentioned in Dr. Bence Jones's "Life of Faraday."

MEETINGS FOR THE WEEK.

- MONDAY, 17th.—Society of Arts, 8. (Cantor Lectures). "Personal Jewellery from Prehistoric Times," by Cyril Davenport.
- TUESDAY, 18th.—Royal Institution, 3. "The Cell—its means of Offence and Defence—Immunity," by Allen Macfadyen, M.D., B.Sc.
Society of Arts, 4.30. "The French-Canadian Relationship to the Crown," by W. T. R. Preston.
- WEDNESDAY, 19th.—Society of Arts, 8. "The Use of Balloons in War," by Eric H. Stuart Bruce, M.A.
Chemical, 5.30. Ballot for the election of Fellows. "Enzyme Action," by A. J. Brown.
"On the Velocity of Hydrolysis of Starch by Diastase, with some remarks on Enzyme Action," by H. T. Brown and T. A. Glendinning.
"Polymerisation Products from Diazoacetic Ester," by O. Silberrad. "Condensation of Phenols with Esters of Unsaturated Acids" (Part VII.), by S. Ruhemann and H. E. Stapleton. "The Union of Hydrogen and Oxygen," by H. B. Baker.
- THURSDAY, 20th.—Royal Institution, 3. "The Scot of the Eighteenth Century—III. With his Books," by the Rev. John Watson, D.D. (Ian MacLaren).
- FRIDAY, 21st.—Royal Institution, 9. "Musical and Talking Electric Arcs," by W. Duddell.
- SATURDAY, 22nd.—Royal Institution, 3. "Some Electrical Developments," by Lord Rayleigh, M.A., F.R.S., &c.

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PHYSICS.. .. R. A. LEHFELDT, D.Sc.
CHEMISTRY.. .. J. T. HEWITT, D.Sc.
ENGINEERING (Mech.).. .. D. A. LOW, M.I.M.E.
ENGINEERING (Elec.).. .. J. T. MORRIS, A.Inst.C.E.

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J. AUSTIN JENKINS, B.A.,

February 4, 1902.

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Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896). Alfred Jörgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

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THE CHEMICAL NEWS.

Vol. LXXXV., No. 2204

THE STRATIFICATIONS OF HYDROGEN.*

By Sir WILLIAM CROOKES, F.R.S.

THE following pages give the outcome of attempts to prepare pure hydrogen, and experiments on the stratifications exhibited by the purified gas under the influence of an induction current. The researches were commenced in 1884, and have been continued intermittently to the present time.

The original apparatus consisted of a vacuum tube of soda-glass, 6 inches long and $\frac{1}{2}$ inch wide, having sealed-in

tubes attached to the apparatus. A portion of the palladium was now gently heated; the gauge sank 12 c.m., when it was again well exhausted and a little more hydrogen liberated. This was repeated three times, when the tube was exhausted to the stratification-point—about 4 m.m.

Parti-coloured Stratifications.

The strata were twelve in number, and of a slightly concavo-convex button-shape, each of a blue colour on the convex side facing the negative pole, and pink on the other side. On reversing the current, the buttons faced round, always presenting the blue face to the negative pole. Examination with a spectroscope showed strong hydrogen lines in the pink parts, and both hydrogen and mercury in the blue parts. Fig. 1 shows the appearance at this stage.

The exhaustion was now raised to 2 m.m., when the whole of the blue faces of the parti coloured buttons suddenly migrated to one bright blue, well-formed button, nearest the negative pole all the other buttons remaining

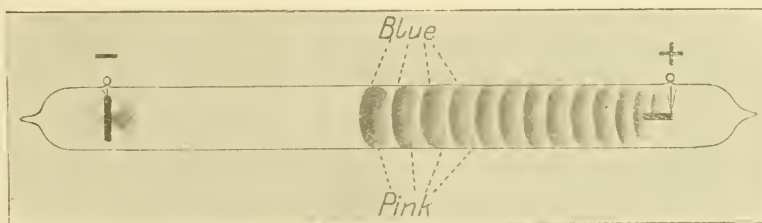


FIG. 1.

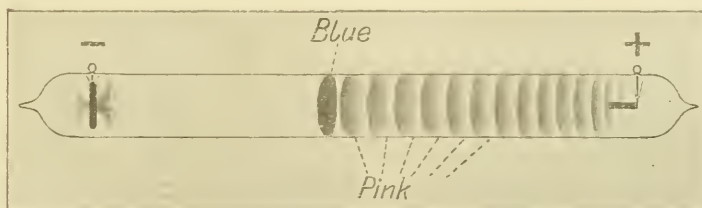


FIG. 2.

aluminium terminals at each end. The pole at one end was ring-shaped, at the other pointed. The vacuum tube was connected to the mercury pump at one end, a tightly packed phosphoric anhydride tube intervening. At the other end was another phosphoric anhydride tube, a hydrogen generator of zinc and dilute sulphuric acid, and a tap to control the flow of gas. The hydrogen was passed through the apparatus for some hours, and the whole was exhausted to a high point, re-filled, and again exhausted. This was repeated many times; but, on exhausting to the stratification-point, I could get no spectrum which did not show, in addition to hydrogen, also mercury.

The apparatus was therefore modified. Strips of palladium foil were charged with hydrogen by the electrolysis of dilute sulphuric acid; a 4-cell Grove's battery being used for one hour. After drying, the palladium strips were put in a glass tube, and sealed between the generator and vacuum tube. At first, crude gas from the generator was used to wash out the apparatus, and after many fillings and exhaustions—the last to the highest possible point—the generator and tap were sealed off, leaving only the palladium and drying

pink. The appearance is shown in Fig. 2. Round the negative pole an indistinct halo showed both mercury and hydrogen; but on the blue button mercury only was detected, not a trace of even the brightest hydrogen line being there seen. On the pink portions the hydrogen lines were in excess, but mercury could be seen all along the tube.*

* I have been unable to find any reference to this concentration of the blue constituents of the strata into one single button at the end near the negative pole. In the classical researches of Messrs. De la Rue and H. W. Müller on the "Electric Discharge with the Chloride of Silver Battery," numerous references are made to the blue and pink parti-coloured character of the strata, and also to the change of colour from all blue to all pink which follows a change in the electrical conditions. Thus we read:—"Thirty-nine strata, the convex side being blue and the broader concave side reddish." "Twenty-one strata, very blue on the convex face, pink on the concave."—*Phil. Trans.*, vol. clxix, p. 175.

Sometimes the stratifications are described as all of one colour:—"Twenty-one very blue strata." "The strata were blue, and sixty-one in number." "Showing twenty-one double strata, intensely blue, but with a carmine line between the components."—*Phil. Trans.*, vol. clxix, pp. 175, 190.

Frequently a change from all of one colour to all of the other colour is recorded. Thus:—"The tube was filled to within 1 inch of the negative with strata; all these were blue, but they turned pink when 200,000 ohms resistance was introduced. When 7,500,000 ohms resistance was introduced, a very close and somewhat agitated pink stratification was produced." "Thirty-four steady blue strata were

* A Paper read before the Royal Society, February 6, 1902.

At 1 m.m. pressure very little hydrogen could be detected by the spectroscope, the stratifications had almost disappeared, and mercury was strong throughout the tube.

Elimination of Mercury Vapour.

The mercury apparently diffused into the tube from the pump and many devices were adopted to keep it out. Long glass tubes filled with purified sulphur broken into coarse pieces were partially successful, but something (probably sulphur) was communicated to the hydrogen which interfered with the purity of the colours. Also the sulphur did not prevent a little mercury diffusing in if the tubes were left on the pump all night.

Experience showed that mercury was very difficult to eliminate from a tube once it had gained access. It adheres to the walls of the tube, and defies detection in the cold, but becomes visible in the spectroscope as soon as the tube is heated by a lamp. Therefore a new hydrogen tube was made, and connected with tubes containing sulphur, bright copper turnings, and phosphoric

to the front on increasing the vacuum; the single blue button showing the mercury spectrum. Continued pumping diminished the hydrogen, but apparently did not affect the mercury to the same extent. It appears that the great diffusibility of the hydrogen causes it to be readily pumped out, whilst the mercury is continually being replenished by diffusion from the pump.

A slight difference is produced in the purity of the colours of the strata according as aluminium or platinum poles are used. A pair of vacuum tubes was made, one having the usual shaped aluminium poles, the other having platinum poles of a special construction. Each terminal was of double wire, at one terminal bent into the form of a ring, and at the other a straight pole. The ends of the wires forming the poles were sealed through the tube close together but not touching, and terminated in loops outside, so that they could be raised to red or white heat by connecting them with a few battery cells. The arrangement will be readily understood by reference to the accompanying drawings (Fig. 3). Thus heat could easily



FIG. 3. (Full size).

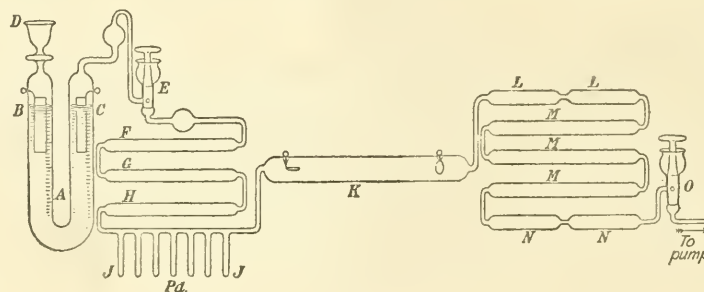


FIG. 4.

anhydride; the copper intervening to keep out the sulphur. Here, again, mercury was detected after some days, but only in minute traces. In each of these cases occurred the phenomena of the pink and blue strata at one exhaustion, changing to all-pink with a concentration of the blue

produced; on introducing 200,000 ohms resistance, the strata turned pink." "With 3600 cells the strata were blue and sixty-one in number. With 700,000 ohms resistance the strata were reduced to eighteen and turned pink." "A change of current frequently produces an entire change in the colour of the strata. For example, in a hydrogen tube, from a cobalt-blue to a pink."—*Phil. Trans.*, vol. clxix., pp. 183, 190, 231.

Very few spectrum observations were made by the authors, and they are not very definite in character. One tube, which gave ten luminosities, was examined with the spectroscope. "The C and F lines were brilliantly seen in the glow around the negative terminal, but were not visible in the spectrum of the nebulosities, notwithstanding that they were brighter than the negative glow; there were blue, green, and red visible, but not the characteristic green and red lines of hydrogen." In another tube, "The characteristic hydrogen lines were very brilliant when the spectroscope was directed to the glow around the negative terminal, but quite a different spectrum was seen on a bright stratum, with mercury lines in the orange." "The hydrogen lines could not be seen either in the strata or the glow on the negative ring, but instead of them mercury lines came out strongly. There is reason to think that at this stage there was little gas except mercury vapour in the tube." "A change of current frequently changes the spectrum of the strata; moreover, the spectra of the illuminated terminals and the strata differ."—*Phil. Trans.*, vol. clxix., pp. 180, 216, 232.

be applied during exhaustion, first to one pole and then to the other, even while the induction spark was passing. At first much gas was liberated from the platinum, but by repeated heating, pumping, and passing the spark, all the occluded gas was abstracted, and then the fillings with hydrogen and subsequent operations were commenced.

The general plan of the apparatus is shown in the drawing (Fig. 4). At the end furthest from the pump is the hydrogen generator, A, consisting of a U-shaped tube filled with dilute sulphuric acid, having in one leg a plate of amalgamated zinc, B, and in the other a sheet of platinum, C. Both the platinum and the zinc are connected metallically to platinum wires sealed through the glass. A funnel with a stopper, D, sealed to the outer limb of the generator admits dilute acid when required. A tap, E, on the other limb enables the reservoir of hydrogen to be disconnected from the rest of the apparatus. Following this tap is a battery of three tubes, one F, containing small lumps of dry caustic potash; the second, G, and the third, H, tubes containing phosphoric anhydride. Between the second phosphoric anhydride and the vacuum tube is another tube having sealed on to it, comb-like, seven projecting arms, J, each containing a strip of palladium foil saturated with hydrogen.

The vacuum tube, K, is 8 inches between the terminals

and $\frac{3}{8}$ inch diameter; it comes next to the comb, and then between it and the pump is a battery of tubes, each 12 inches long, to keep out the mercury. The first tube, L, is divided by a constriction in the middle, and contains, in the half next the vacuum tube, bright metallic copper, in the other half sulphur. The three next tubes, M, M, M, contain sulphur, but in the middle of each are placed a few grains of iodine separated from contact with the sulphur by a plug of asbestos on each side. The sulphur is prepared by keeping it fused at a temperature a little below its boiling-point till bubbles cease to come off, so as to get rid of water and hydrogen compounds. It is then allowed to cool, and is pounded and sifted so as to get it in the form of granules, averaging a m.m. in diameter. Ignited asbestos is packed at each end of the tubes to keep the contents from blowing out when the vacuum is proceeding, or air is suddenly let in.* Next follows a tube, N, N, constricted in the middle, containing in the first half phosphoric anhydride, and in the second finely powdered dry caustic potash. A tap, o, connects the apparatus with the pump to prevent diffusion of mercury when the pump is not in use. All parts of the apparatus were built up in place and sealed together with the blowpipe. The glass was new, and the apparatus had been kept apart from mercury until it was sealed together.

The apparatus was exhausted from air, the tap E being closed and D open. Electrolysis was then commenced (D being closed), and the tap E was slightly turned until the escape of hydrogen into the apparatus was equal to the speed of its generation. The apparatus was filled, and several times exhausted, until no improvement in the spectrum or stratifications could be seen. The electrolytic cell was then sealed off at a narrow constriction between the first potash tube, F, and the phosphoric anhydride tube, G. After good exhaustion one of the branch tubes of palladium was heated, when the gauge sank several centimetres. Exhaustion and re-filling from fresh palladium were repeated until no alteration was detected in the appearance of the strata. Then, for the first time, I obtained hydrogen strata showing no blue, either throughout the tube or concentrated in front, whilst the most careful examination showed no mercury. The stratifications were all pink, and showed the hydrogen lines strongly.

Many disadvantages were noticed in the apparatus just described, the chief being the danger of introducing more impurities than were kept out by the copper, sulphur, and iodine tubes. The palladium method of introducing hydrogen was not altogether satisfactory, as only small quantities could be dealt with, and occasionally at a critical point the store was exhausted. Also, the electrolytic generator of hydrogen was too small. It was decided, therefore, to devise and fit up an entirely new piece of apparatus. In this another method was used for keeping out the mercury. It had been noticed that the diffusion of mercury from the pump proceeded the more slowly as the distance from the pump and the narrowness of the connecting tubes increased. It was thought that by introducing a long narrow spiral between the pump and the apparatus, one complicated system of tubes, with their attendant dangers, could be removed; the result showed this supposition to be correct. Two vacuum tubes were employed, one having aluminium the other platinum terminals. The hydrogen generators were increased in size and number, and were so distributed that they could be sealed off one after the other during the progress of the experiment.

(To be continued).

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART XI.

By HARRY BREARLEY.

(Continued from p. 79).

COPPER.

III. VOLUMETRIC ESTIMATIONS.

a. Cyanide Process.—

1561. FIELD (C. N., i., 25, &c.).—Not necessary to filter off precipitated $\text{Fe}_2(\text{HO})_6$. Arsenic easily separated from KCN solution. Hg, Ag, Zn, Ni, Co, and Mn interfere. Describes also the following methods:—Titration with alkaline sulphide (Pelouze); Reduction to Cu_2O and titration with permanganate (Treille); precipitation with sugar and titration with permanganate (Mohr); titration with Fe_2Cl_6 and KMnO_4 (Schwarz); precipitation of Cu with Fe and estimation in various ways; titration with KI and $\text{K}_2\text{Cr}_2\text{O}_7$ (Streng); estimating metal used in reducing CuO to Cu_2O ; the iodide process; colour comparison of AmHO solutions; weighing as $\text{Cu}_2\text{S} + \text{CuO}$; and the sulphocyanide process (Rivot).
1562. FLECK (C. N., ii., 35).—Results vary with excess of AmHO; uses Am_2CO_3 instead, and an indicator for end-reaction.
1563. STEINBECK (C. N., xix., 207).—Precipitate Cu from solution of ore with Zn and Pt, dissolve in HNO_3 , and titrate. Influence of Pb, Zn, AmHO compounds and heat observed.
1564. THOMSON (C. N., xxxiii., 152).—Observes influence of many elements on titration; that of Zn, Cd, Mn, Ni, Sn, Hg, Ag, Au, Pt, and Pd most pronounced. AmHO and its salts cause variations.
1565. ULBRICHT (C. N., xlv., 82).—Sample to be treated exactly as standard, and to be as nearly as possible identical.
1566. BERINGER (C. N., xlviii., 111).—Results influenced by mode of operation and temperature. AmHO exerts same influence whether as sulphate, nitrate, or chloride. Soda salts no influence, except carbonate, sulphite, and nitrite. Determines conditions under which proportional results are obtained.
1567. DAVIES (C. N., lviii., 131).—Results are more concordant when the solution is made alkaline with Na_2CO_3 instead of AmHO.
1568. FESSENDEN (C. N., lxi., 183 and 253).—Confirms 1567; the end-reaction is more decided.
1569. BREARLEY (C. N., lxxvi., 189).—The AgI indicator (580) is applied to the KCN estimation. The results are better, particularly when the solution is made alkaline with Na_2CO_3 .
1570. BREARLEY (C. N., lxxvi., 291, 303).—Influence of many elements on 1569 process observed. Interference of Zn, Mn, and Cd avoided; Cr_2O_3 salts injurious. Organic acids and pyrophosphate used to keep precipitable bodies in solution.
1571. DONATH and TELLER (C. N., lvii., 102).—Ore ignited with Zn powder, boiled with H_2SO_4 , Cu dissolved from associated gangue with HNO_3 , and titrated with KCN.
1572. JOHNSON (J. S. C. I., 1889, 603).—Cu precipitated from solution of pyrites with KCN and SnCl_2 , dissolved in nitrohydrochloric, and titrated with KCN; or the CuCNS dissolved in $\text{Fe}_2(\text{SO}_4)_3$ and resulting FeO titrated with KMnO_4 . SnCl_2 is better than any other reducer.
1573. ELLIS (J. S. C. I., 1889, 686).—Tabulated results showing influence of zinc. The solution may stand an indefinite time after adding AmHO without spoiling.
1574. CLENELL (J. S. C. I., 1900, 14).—Cu in KCN solutions estimated by adding H_2SO_4 until a precipi-

* An apparatus of this kind was briefly described by the author in a paper read before the Royal Society in 1885 ("Radiant Matter Spectroscopy—Part II., Samarium," *Phil. Trans.*, vol. cixxvi., p. 693, June 18, 1885). The apparatus was used to prevent mercury from getting into the small radiant-matter tubes employed in the research.

tate of $\text{Cu}(\text{CN})_2$ appears, then an excess of H_2SO_4 , and finally titrating the free acid in a fraction of the filtrate with Na_2CO_3 . (See also 1580).

b. Iodide Process.—

1575. WESTMORELAND (*J. S. C. I.*, 1886, 48).—Analysis of ores, pyrites, &c. Neither Ag, Zn, Cd, As, Bi, Mn, or Sn interfere; nor does Fe materially in the presence of Na_3PO_4 or As_2O_3 . Also critical account of the electrolytic and dry assay processes and the assay of Au in bar Cu.
1576. WESTMORELAND (*C. N.*, lviii, 76, 108, and 132).—Shows that the iodide process is superior to the electrolytic for all kinds of Cu compounds.
1577. WILLIAMS (*C. N.*, lviii, 272).—Pb and As exert a prejudicial effect on the titration.
1578. HAUPT (*C. N.*, lxx, 206).—Titration not interfered with by Zn or Pb; it is by Ni and Fe. Cu precipitated from Fe solutions with Zn. KI detects one Cu in 500,000. Experiments on the ignition of Cu_2S .
1579. BRUYN and VAN LEENT (*J. C. S.*, lxii, 753).—Operate in stoppered flasks. Ni, Mn, and Fe as sulphates and free acid no not interfere; Bi does.
1580. DULIN (*C. N.*, lxxii, 70).—Describes KCN method and its limitations. KI process influenced by large amounts of alkaline salts and Bi. For either titration first precipitate Cu with Al. Electro-deposition from solutions containing much HNO_3 .
1581. LOW (*C. N.*, lxxiv, 52).—First precipitate Cu with Al; then neither Ag, Pb, Bi, or As interfere. Procedure for ores.
1582. WILLENS (*C. N.*, lxxvi, 243).—KI process applied to estimation of Cu in pyrites.
1583. SHELBY (*J. S. C. I.*, 1900, 776).—FeO formed by hypo. and then sheet Zn added. Nascent H and the previously liberated S form H_2S , which precipitates the Cu. Estimation with KI or KCN after dissolving in HNO_3 , &c. (See also 1591).

c. Various Volumetric Processes (see also 1572).—

1584. FLEISCHER (*C. N.*, xix, 206).—Precipitate as sub-iodide with KI and SnCl_2 , dissolve precipitate in $\text{Fe}_2(\text{SO}_4)_3$, and titrate FeO with KMnO_4 . Or, precipitate Cu with KCNS and SO_2 , digest CuCNS with NaHO , and estimate Cu_2O as before. Pb, Ag, and Hg are the only interfering metals, and these are separated with H_2SO_4 , HCl , and SnCl_2 respectively.
1585. HENRIQUES (*J. C. S.*, lxiv, ii, 345).—Precipitate with SO_2 and standard KCNS. Estimate excess KCNS with AgNO_3 and $\text{Fe}_2(\text{SO}_4)_3$ indicator.
1586. MEADE (*C. N.*, lxxx, 67).—Decompose precipitated CuCNS with KHO , add collected $\text{Cu}_2(\text{OH})_2$ to acid $\text{Fe}_2(\text{SO}_4)_3$ and titrate FeO with KMnO_4 .
1587. PARR (*J. S. C. I.*, 1900, 1148).—Decompose CuCNS with NaHO , destroy $\text{Cu}_2(\text{OH})_2$ with KMnO_4 in alkaline liquid, then acidify and titrate KCNS with KMnO_4 . 1 c.c. $\text{N}/10 \text{ KMnO}_4 = 0.0009 \text{ Cu}$.
1588. CAVEN and HILL (*J. S. C. I.*, 1897, 981).—Add Cu_2O to excess KMnO_4 in H_2SO_4 and titrate un-reduced portion with oxalic acid.
1589. DEDERICH (*J. C. S.*, lxxvi, ii, 813).—Digest HNO_3 solution of brass with NaHSO_3 , add standard AmCNS , and titrate excess with AgNO_3 in aliquot filtrate.
1590. ZECCHINI (*J. S. C. I.*, 1899, 710).—Add excess of solution containing hypo. and AmCNS and titrate with iodine. Neither AmCNS nor CuCNS react with iodine.
1591. GARRIGUES (*C. N.*, lxxvii, 41 and 52).—End-point of iodide process sharper in H_2SO_4 than in $\text{C}_2\text{H}_4\text{O}_2$ solution. Decompose precipitated CuCNS with standard NaHO and titrate excess with acid and methyl-orange. Con-

joint presence of Zn and Sb interfere. Some important points in the analysis of bearing-metals, bronzes, &c.

1592. WEIL (*C. N.*, xxiii, 49; and xlvii, 284).— HCl solution of Cu titrated at boiling-point with SnCl_2 to decolorisation. HgCl_2 may be used as indicator. Fe and Ni interfere.
1593. JEAN (*J. C. S.*, lxiv, ii, 493).—Estimation of Cu, Fe, Sb, and Zn in minerals by Weil's process.
1594. KUNSEL (*C. N.*, viii, 38).—Titrate hot AmHO solution with Na_2S , using freshly precipitated ZnS as indicator. Ni or Zn do not interfere. JEAN (*C. N.*, lxxvii, 172) uses PbCO_3 paper as indicator; the process separates As. BORNTÄGER (*J. C. S.*, lxvii, ii, 120) uses a ferrocyanide indicator, and says Cu-Zn alloys may be thus titrated.
1595. CASAMAJOR (*C. N.*, xlv, 167).—Titration of AmHO solutions as in 1594 until blue colour goes is inaccurate. Precipitates instead from alkaline tartrate solutions until no further cloud forms. Same process for Pb, &c.
1596. BALLING (*C. N.*, xlvii, 248).—The sulphide of Cu (Pb, Zn, or Hg) is digested with AgNO_3 and excess Ag titrated with KCNS.
1597. LUCKOW (*J. C. S.*, lxiv, ii, 242).—Titration of Cu-Sn-Sb alloys with ferrocyanide. RANTER (*J. C. S.*, lxx, i, 3).—The precipitate always retains $\text{K}_4\text{Fe}(\text{CN})_6$. SPICA (*J. C. S.*, lxx, ii, 127) uses Fe_2Cl_6 indicator.
1598. QUESSAND (*J. C. S.*, xlviii, 441).—Precipitate with slight excess of $\text{K}_4\text{Fe}(\text{CN})_6$, and then measure the alkaline solution of Rochelle salt needed to destroy the precipitate.
1599. DONATH and HATTENSAUR (*J. S. C. I.*, 1890, 554).—Cu precipitated with ferrocyanide from alkaline tartrate solutions. Fe should be present, so that end-reaction (blue) may be noted by adding acetic acid to test drop.
1600. BERNTHSEN (*C. N.*, xliii, 79).—Titrate cupric solution with hypo. in an atmosphere of H. When colour is nearly gone add indigo to heighten end reaction.
1601. LAGRANGE (*C. N.*, xxx, 241).—Precipitate with KHO , convert to tartrate, and reduce to Cu_2O with standard glucose.
1602. MULLER (*C. N.*, xxxi, 143).—Measure volume of H needed to reduce CuO to Cu in a closed tube.
1603. VITALI (*J. C. S.*, lxviii, ii, 140).—Mix CuSO_4 with KI and starch, add H_2SO_3 to decolorise, and estimate liberated H_2SO_4 with standard alkali.
1604. ETARD and LEBEAU (*C. N.*, lxi, 137).—Add hydrobromic acid to concentrated solution, and then standard SnCl_2 until the violet colouration is discharged.
1605. PURGOTTI (*J. C. S.*, lxxii, ii, 349).—Boil solution with excess NaCl and hydrazine sulphate. The evolved N is measured at normal temperature and pressure.
1606. LESCŒUR (*J. C. S.*, lxxiv, ii, 484).—Cu is precipitated as oxide, dissolved in excess acid, and titrated back with alkali. Cu_2O obtained with glucose titrated simultaneously. See also RUOSS (*J. C. S.*, lxxiv, ii, 644).

IV. COLORIMETRIC ESTIMATIONS.

1607. CARNELLEY (*C. N.*, xxxii, 308).—The colour formed with ferrocyanide in neutral solution is compared with standards. AmNO_3 , &c., heighten the colour. Many alkaline and earthy salts do not interfere. Detects (so does H_2S) 1 part in 1,500,000. See also ILES (*C. N.*, xxxiv, 16) and BLUNT (*C. N.*, xxxiii, 7).
1608. LUCAS (*C. N.*, lxxix, 67).—Process 1607 used for estimating O in Cu and Cu in Fe. Separation of

Fe and Cu not complete after several re-precipitations.

1609. MUIR (C. N., xxxiii., 11).—Add H_2S and compare with standards. Determines minimum and maximum which can be estimated thus.
1610. HEATH (C. N., lxxvi., 184).—Comparison of AmHO solutions. Permanent standards prepared from $CuSO_4$. See 1538.

V. DETECTION.

1611. BELLAMY (C. N., xx., 228).—An alcoholic tincture of campeachy wood detects 1 part Cu (or Fe) in 20,000,000 parts of water.
1612. WAGNER (C. N., xlv., 35).—Limits of following tests are:—Ferrocyanide, 1 in 200,000; AmHO, 1 in 25,600; xanthogenate, 1 in 900,000.
1613. ALIAMET (C. N., lvi., 160).—Pyrogallic acid in saturated Na_2SO_3 gives red colour with Cu. (C. N., lviii., 293).—Test by no means characteristic.
1614. CAILLETET (C. N., xli., 160).—Add pyrogallic acid in ether to the oil; a brown colour = Cu.
1615. ANON. (C. N., xliii., 117).—One one-hundredth m.grm. Cu can be detected by the HBr test.
1616. DENIGES (C. N., lix., 168; and *J. C. S.*, lxxviii., ii., 330).—A more stable form of reagent for above test is saturated KBr in H_2SO_4 .
1617. SABATIER (*J. S. C. I.*, 1894, 1092).—KBr and H_3PO_4 may be used instead of HBr. Detects one-tenth m.grm. Cu.
1618. KERN (C. N., xxxiv., 78).—Precipitate acid solution of iron with AmHO, acidify evaporated filtrate, and add Mg. Traces of precipitated Cu observed with the microscope.
1619. WOODCOCK (C. N., xxxvi., 240).—Precipitate Cu with Zn-Pt element; expose Pt to Br+HBr; the violet colour detects 0.001 m.grm. Cu.
1620. JAWOROWSKY (*J. C. S.*, lxxii., ii., 285).—Shake AmHO solution with phenol; with traces of Cu, solution becomes turbid and blue.
1621. BACH (*J. S. C. I.*, 1899, 401).—Mixture of formaldehyde and hydroxylamine hydrochloride gives violet colour with one part Cu in a million.
1622. CAZENEUVE (*J. C. S.*, lxxviii., ii., 627).—Diphenylcarbazide in benzene gives a violet colour when shaken with a cupric solution.
1623. LENOBLE (*J. C. S.*, lxiv., 554).—Potassium mercuric iodide throws down bright red precipitate from cupric solutions.
1624. THOMS (C. N., lxiv., 190).—Depends on yellow colour formed with KI. One part in 200,000. See 1578.
1625. GERLAND (C. N., ix., 73) and CHAPMAN (C. N., xii., 231).—Blowpipe tests for Cu.
1626. SCHIFF (C. N., i., 191) and ORLOWSKI (C. N., xlvii., 24).—Tests for cuprous oxide.

VI. MISCELLANEOUS.

1627. THOMSEN (C. N., xxxix., 185).—Precipitate formed with H_2S is not CuS , but a mixture of S and a lower sulphide. See also COPPOCK (C. N., lxxiii., 262; and lxxvi., 231) and BRAUNER (C. N., lxxiv., 99).
1628. ANON. (C. N., xlv., 120).— $Cu(NO_3)_2$ mixed with PbA_2 is dissolved by NaHO and not re-precipitated on boiling.
1629. DEBRAY (C. N., xlvii., 304).— CuS is dissolved in considerable quantities by Am_2S if Mo is also present.

The following refer to papers which deal generally with the estimation of the impurities of commercial copper:—

1630. ABEL and FIELD (C. N., iv., 264); ABEL (C. N., ix., 124); FRESSENIUS (C. N., xlvii., 18); KUHN (*J. S. C. I.*, 1884, 374); JEAN (*J. S. C. I.*, 1896, 677); HAMPE (*J. S. C. I.*, 1894, 421; and 1897, 1043); KELLER (*J. C. S.*, lxxviii., ii., 166); WARREN

(C. N., lv., 62; and lxxiii., 37); BENNEVILLE (*J. C. S.*, lxxvi., ii., 297 and 298); MURMAN lxxii., ii., 346); HOLLARD (*J. S. C. I.*, 1897, 166 and 763; and C. N., lxxxi., 258), electrolytic; CLARK (*J. S. C. I.*, 1900, 27); ULKE (*J. S. C. I.*, 1900, 170).

The following deal with the estimation of As in Cu:—

1631. CLARKE (*J. S. C. I.*, 1887, 353); PLATTEN (*J. S. C. I.*, 1894, 324); PATTINSON (C. N., xlv., 136); HEATH (*J. S. C. I.*, 1897, 699).

The following deal with the estimation of O in Cu:—

1632. AUBEL (C. N., xix., 238); SABATIER (*J. C. S.*, lxxii., ii., 261); ANON. (C. N., xxxvi., 241); LUCAS (C. N., lxxx., 86); DEWEY (*J. S. C. I.*, 1889, 134); BLOUNT (*J. S. C. I.*, 1896, 296); ARCHBUTT (*J. S. C. I.*, 1900, 1148). The estimation of O is also dealt with in many papers under 1630.
1633. WHITEHEAD (*J. S. C. I.*, 1895, 513).—Fe in Cu.
1634. SMITH (C. N., lxxii., 76).—Au and Ag in copper. See also 1575.

(END OF PART XI.).

ON RADIO-ACTIVE LEAD.

By F. GIESEL.

FROM a large quantity of the mother-liquor of barium-radium bromide resulting from the technical working of about 2000 kilogrms. uranium ore, I had separated (by means of ammonia and consequent purifying with sulphuric acid) about 3 m.grms. of an intensely radio-active substance which behaved like lead, and resembled preparations of radium in its action (compared on the phosphorescent screen). My interest in the substance increased when I found unexpectedly, after a year had elapsed, that it still exhibited strong radiation. I therefore gladly welcomed Demarcay's proposal to undertake an exact spectral examination.

As the small residue of sulphide (about 1 m.grm.) could not easily be separated mechanically from the small filter, the latter was ignited (with the substance), and evaporated with concentrated hydrochloric acid. The resulting compound, which consisted of crystals resembling lead chloride, was sent to M. Demarcay.

I received from him on December 11th, 1901, the following communication:—

"Your substance influences the platinocyanide screen.

"The spectrum of the hydrochloric acid solution was principally that of lead, which must form the bulk of the substance.

"There are traces present of calcium, barium, strontium, chromium, aluminium, manganese, bismuth, tin, slight traces probably of molybdenum, also of yttrium perhaps arising from my laboratory; magnesium in marked degree; iron to a remarkable extent.

"These substances represent the sum total of the lines of known origin, the strong, predominating, weak, and very weak, with the exception of two lines, also very weak, but not to be passed over. They cannot be identified amongst those of known origin.

"One of the lines, λ 3659.6, occurs with an extremely weak iron line. It also coincides with a line of the air spectrum, which is very weak.

"I do not believe that this line belongs either to the iron or the air, or to both; without, however, wishing to assert this positively.

"The second extremely weak line, λ 4116.8, which stands next to a strong line of platinum, cannot be identified with any other.

"I attach a certain importance to these two lines, particularly on account of the unexpected absence of radium. Its lines are absolutely wanting. If it is pre-

sent it must be so in very small quantity. It may possibly be that the radio-activity of your substance arises from a hypothetical body, which gives these two lines and some of the infinite number of weak ones, which have not been mentioned."

This examination admits of another explanation of the radio-activity of my substance (as well as that given by M. Demarçay above), viz., that ordinary active lead is there, induced by radium. Though according to experiences hitherto obtained the induced activity of bodies is relatively soon lost, it is yet possible that under the existing circumstances—minute quantities of lead, large quantities of radium, the long time of exposure to its influence, viz., one year—the resulting activity of the lead might be of longer duration as well as of greater intensity.

This should be determined by research.

A decomposition into active and less active portions by chemical processes would not contradict these deductions, as I have convinced myself that ordinary lead with activity induced by radium becomes thus enriched. Debierne has already established this fact in the case of barium made active by actinium.

Hofmann and Strauss will see in the assumption of a new element and the above examination a confirmation of the identity of my substance with their "radio-lead," in order to enforce the conclusion of their latest publication, which runs:—"We are the first to have demonstrated the existence of a radio-active body closely allied to lead."

This statement necessitates the following explanation. I have shown that the Becquerel radiation of "radio-lead" is very slight, being considerably weaker than that of the pitchblende, which is the starting-point. The relatively strong action of the sulphate after only fifteen hours through the glass of the photographic plate is caused solely by the phosphorescence light of this substance; hence the negative result with the chloride, sulphide, &c., which either phosphoresce not at all, or insufficiently. If these light rays are kept back, after thirty hours no action takes place, and this only occurs after five days with glass 1·2 m.m. thick. Hofmann and Strauss consider the blackening of the photographic plate, not caused apparently by the action of light, as the result of the action of the Becquerel rays, and denote the substance thus tested as radio-active, as may be gathered from many examples in their publications. Hence none of these statements referring to the action through the glass of the plate are any criterion for radio-activity, because it is a question of radio-active substances. I first demonstrated that the phosphorescence light of the Becquerel rays is exhibited constantly; hence also the illusion of Hofmann and Strauss concerning the "latent-activity."

Let us add, for the better judgment of the strength of the activity of "radio-lead," that the first polonium preparations of Curie's were several hundred times as active as pitchblende. The Curies say in their paper that the new radio-active substances, including polonium and actinium, are at least 100,000 times as active as metallic uranium. (The ratio of metallic uranium to pitchblende is about 2:7). If, therefore, Hofmann and Strauss assert that the activity of "radio-lead" is only superseded by radium, they are quite mistaken. Even if it is allowed that the preparations left over for me to examine were only one-third of the strength of the newest, yet the intensity of the Becquerel radiation would be three times that of pitchblende at the most.

Accordingly, if "radio-lead" contains besides lead a strongly radio-active body, there can only be small traces of the latter. Under these circumstances it is incomprehensible how an atomic weight could be found widely differing from lead!

The determination of the "distinct spectral lines in the violet" is of the greatest importance for the existence of a new radio-active substance in "radio-lead." Spectrum analysis would also give the quantity of the new substance assumed by Hofmann and Strauss in their "radio-

lead preparations," which they first looked upon as nearly pure, and tried to fit into the periodic system on the ground of their atomic weight determinations.

As my substance does not exhibit the same spectrum line, an identity with "radio-lead" is therefore excluded; and, in this respect, only an exact measurement of the "radio-lead" spectrum can procure certainty.

The simple fact that lead chloride and lead preparations from uranium ores are weakly active has long been known by Hofmann and Strauss, and also announced by them. On the other hand, the publications of the latter on "radio-lead," also on "radio-active lead," are so uncertain, and the results so confused in consequence of many alterations, that clearness on this side is desirable. Before this is done, the statement of Hofmann and Strauss quoted above, as well as their claim to priority, are futile.—*Berichte Deutschen Chemischen Gesellschaft*, January 18, 1902.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, February 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month shows a very serious deficit; the amount of rain measured was only 0·66 inch, the average for thirty-five years is 2·08 inches, leaving a deficit of 1·42 inches, or 68 per cent on the thirty-five years' average.

Our bacteriological examinations of 565 samples have given the results recorded in the following table; we have also examined 48 other samples, from special stand-pipes, wells, &c., making a total of 613 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	231
New River, filtered (mean of 140 samples) ..	15
Thames, unfiltered (mean of 27 samples) ..	4396
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 309 samples)	30
Ditto ditto highest	258
Ditto ditto lowest	0
River Lea, unfiltered (mean of 27 samples) ..	233
River Lea, from the East London Company's clear-water wells (mean of 35 samples) ..	7

Of the 484 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 20 samples, or 4·1 per cent, were sterile. Nine samples contained more than 150 microbes, while thirty samples, or 6·1 per cent, contained over 100 microbes per c.c. The mean number of microbes in the thirty excess samples was 143, against a corresponding mean of 185 in twenty-seven excess samples during December.

The impounding and filtration have been very satisfactory considering the time of year, and the extraordinary drought has prevented the increase in the organic matter which usually is characteristic of the Thames during the winter months.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

ON PYRITE AND MARCASITE.*

By H. N. STOKES.

(Continued from p. 82).

VII. DATA FOR ARTIFICIAL MIXTURES.

The following table gives the results for different mixtures, the numbers in the second column referring to the above-mentioned specimens of pyrite and marcasite respectively.

Values of p for Mixtures of Pyrite and Marcasite.

Per cent pyrite.	Specimens used.	p .	Mean value of p .
0	M 7	16·5	17·3 (18·0)
	M 10	17·4	
	M 12	18·0	
5	P 5; M 7	15·7	16·0
	P 5; M 10	16·5	
	P 5; M 12	15·9	
10	P 5; M 7	15·2	15·2
	P 5; M 10	15·2	
	P 5; M 12	15·9	
20	P 5; M 7	17·3	17·1
	P 5; M 10	16·9	
	P 5; M 12	16·9	
40	P 5; M 7	22·3	22·3
	P 5; M 10	22·2	
	P 5; M 12	29·0	
60	P 4; M 10	29·1	29·0
	P 5; M 7	40·5	
	P 5; M 10	40·2	
80	P 5; M 10	48·9	48·9
	P 4; M 10	48·9	
	P 5; M 10	52·9	
95	P 5; M 10	53·0	52·9
	P 5; M 10	53·0	
100	P 4..	60·3	60·5
	P 5..	60·8	

Discussion of the Curve.

The curve in Fig. 3 is based on the mean values of p thus obtained, with the exception of pure marcasite, where the more probable value 18 is used (see ante).

Influence of the Minimum; Indirect Determination of Small Amounts of Pyrite in Marcasite.—The most obvious features of this curve are the presence of a minimum point when the amount of pyrite reaches about 10 per cent and the increasing steepness as 100 per cent is approached. The minimum implies that a mixture of marcasite with a little pyrite has a less percentage of sulphur oxidised than has pure marcasite. This unexpected result, which is abundantly confirmed by numerous other preliminary data not published, may be partly due to the fact that pyrite uses up more ferric salt than does the equivalent amount of marcasite; the latter is therefore acted on by a solution weaker in Fe^{+++} than if it alone were present, the effect of which is to lower the oxidation co-

efficient. Possibly there may also be an electro-chemical action between the two. A minimum also occurs in the curve for pyrite-galena, while pyrite-chalcocopyrite shows a maximum. The existence of these points shows that it is impossible to predict, from a knowledge of the values of p for any two sulphides, whether the result of the contamination of one with a small quantity of the other will be to raise or to lower the oxidation coefficient. The variation of p from 16·3 to 18 for nearly pure marcasites is presumably due to small amounts of impurities other than pyrite. Practically these have but little effect on the determination of pyrite and marcasite, for, as seen in the table, the three samples of marcasite, though varying from 16·5 to 18, give essentially the same figures when mixed with even as little as 5 per cent of pyrite.

As a result of the minimum, any specimen in which p is about 18 or less may have one of two possible compositions. Which of these is actually present may be tested by adding one-ninth its weight of pyrite and determining the value of p for the new mixture. If depression is produced, the true percentage of pyrite lies to the left of the minimum; if elevation, to the right. In fact, the freedom of a marcasite from pyrite can be regarded as absolutely proved only when this precaution is taken. The determination of p in the original specimen is not necessary; the marcasite in question may at once be mixed with a known amount of pyrite and the original contents of pyrite thus determined. If x represents the percentage of pyrite in the original sample, then a mixture of 90 parts of this with 10 parts pyrite will give—

$$0·9x + 10 = \text{per cent pyrite in mixture.}$$

The latter is found by one determination and the composition of the original sample deduced. An application of this method is given in Section X. (*prox.*) in the case of the marcasites from Garfield Tunnel (No. 20), Littmitz (No. 22), and Crow Branch Mine (No. 23). In the latter two cases the selected material showed no pyrite under a lens, although the specimen as a whole contained it in visible amount.

It further appears from the curve that small amounts of marcasite in pyrite can be determined with greater accuracy than small quantities of pyrite in marcasite. In the former case the determination can probably be made to 1 per cent with duplicate experiments and in the absence of notable amounts of other sulphides; in the latter it can hardly be more accurate than 2 or 3 per cent. It must be remembered, however, that there is a slight uncertainty close to both ends of the curve, due to the unknown influence of minute contaminations. In other cases, however, greater accuracy than is obtainable could hardly be desired.

VIII. INFLUENCE OF IMPURITIES.

When pyrite or marcasite is enclosed in rock, the extraneous material may be removed by digesting with hydrofluoric and hydrochloric acids; but small amounts of insoluble siliceous material can usually be neglected.

Miscellaneous Impurities.

The necessity of extreme care in preparing the material is emphasised above. Since $b > (c-a)$, an inspection of the equation—

$$p = \frac{8·333b}{c-a} - 25$$

shows that the presence of iron salts or oxides, or access of air during the decomposition, affects the ratio—

$$\frac{b}{c-a}$$

in such a manner as to lower the value of p , this effect being greater with pyrite than with marcasite. Free sulphur exerts very little influence, and is, moreover, removed by the preliminary extraction with ether. Without influence are also sulphates, carbonates, or soluble silicates free from iron, insoluble silicates, quartz, and in general

* From the Bulletin of the U.S. Geological Survey, No. 186.

any substance neither contributing iron to nor effecting reduction of the ferric solution. Pyrrhotite and limonite are easily eliminated. Zinc blende, galena, magnetite, and hæmatite, if present in but small amounts and not enclosed in the fine particles of FeS_2 , are more slowly removed by prolonged digestion with hydrochloric acid. All sulphides are more or less readily attacked, and those free from iron, since they do not contribute to $c-a$, should, it might be expected, raise the value of p . If present in traces, they do not appreciably affect the result, but if existing in large amounts, they introduce considerable errors, and abnormal results are to be explained by a qualitative analysis. In reality their influence cannot be always predicted, as pointed out above, and some experiments bearing on this point are given below.

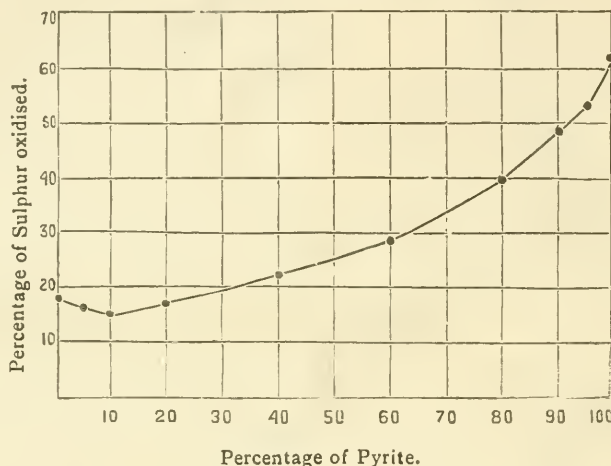


FIG. 3.—CURVE SHOWING OXIDATION COEFFICIENTS OF MIXTURES OF PYRITE AND MARCASITE.

The equation—

$$p = \frac{8.333 b}{c-a} - 25$$

applies, in its original sense of giving the per cent of sulphur oxidised, only to FeS_2 . We may, however, use it in a broader way as simply indicating a certain relation between the permanganate values of the ferrous, ferric, and total iron, and in this sense it may be applied to any sulphide or other compound capable of reducing ferric salts, and is useful in instituting comparisons between these and FeS_2 either alone or in a mixture.

Hæmatite and Magnetite.

The presence of these is indicated during the extraction of the powder with 20 per cent hydrochloric acid if repeated portions of acid continue to be coloured yellow after heating. Difficultly soluble ferric silicates, of course, show the same result. As these iron oxides are scarcely soluble in the weakly acid ferric solution, their presence in small amounts is without appreciable effect.

Galena.

Galena is rather slowly attacked by the ferric solution, and the value of p is infinity. A mixture of galena and pyrite ($p=60.8$) containing 3 per cent lead gave—

$$p = 59.5.$$

From this it appears that small amounts of galena exert a slight depressing influence, and that the curve for galena-pyrite varies from 60.4 to infinity, with a minimum near the pyrite end.

Nickel and Cobalt.

These show a very strongly elevating influence on the oxidation coefficient, as shown by specimens Nos. 27 and 32.

Arsenopyrite.

The action of ferric solution on arsenopyrite, or on pyrites or marcasites containing arsenic in notable amounts, is very characteristic, in that the value of b is always greater than that of c . This is due to the fact that a portion of the permanganate represented by b is consumed in oxidising arsenious to arsenic acid. It may be further observed that in such cases a permanent end-reaction for b cannot be obtained, as the last portions of arsenious acid are oxidised but very slowly in the cold by permanganate. In this event the titration must be stopped at the first change of colour, and since arsenic acid is precipitated very slowly by hydrogen sulphide, it is necessary to conduct the gas through for several hours at a tempera-

ture of about 80° in order to render the precipitation complete and to obtain a correct value for c .

An experiment made with the usual precautions, with carefully selected arsenopyrite gave—

a	..	..	..	..	39.50
b	..	..	..	..	56.90
c	..	..	..	..	45.84

On substituting these permanganate values we get—

$$p = 49.8.$$

The actual sulphur oxidised, as calculated from these figures, assuming that all the arsenic is oxidised to As_2O_3 , is 10.3 per cent, and in fact a notable sublimation of sulphur was observed. The data do not indicate whether any arsenic is liberated, or whether orpiment or realgar is formed, but no evidence of these could be obtained. More elaborate experiments would be required to decide whether under certain conditions they can be formed by the action of ferric salts on arsenopyrite.

A carefully prepared mixture of pyrite and arsenopyrite (2.17 per cent), containing 1 per cent arsenic, was oxidised with the following result:—

a	..	..	..	..	38.33
b	..	..	..	..	43.17
c	..	..	..	..	42.73

The value thus deduced for p , namely, 56.7, corresponds to that of a pyrite containing 2 per cent marcasite. As few pyrites contain as much as 1 per cent arsenic, it appears that in general the presence of arsenic will not interfere greatly with the marcasite determination.

Chalcocite and Bornite.

Chalcocite by itself gives an infinite value for p . The

influence of these minerals on pyrite is stated below. Both are very easily attacked by cold ferric solution.

Chalcopyrite.

As pointed out in the introduction, it is well known that chalcopyrite is more easily attacked by ferric solutions than is pyrite. An experiment with crystallised chalcopyrite, made with the usual precautions, gave—

a	..	..	..	37.44
b	..	..	..	44.01
c	..	..	..	44.11

whence—

$$p = 30.0.$$

From these figures and the determination of the dissolved copper, it appears that not more than 2 per cent of the sulphur is oxidised, and that more copper than iron is dissolved (0.7 atom Fe to 1 atom Cu) from which it may be concluded that pyrite or marcasite is possibly an intermediate product of the oxidation of chalcopyrite by ferric solutions.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 6th, 1902.

Dr. ARMSTRONG, Vice-President, in the Chair.

MESSRS. E. L. Sherwood and A. G. Aston were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederic Guy Stirling Baker, Marryatts Lodge, Snarebrook, Essex; Richard Blenkinsop, Garden Wharf, Battersea, S.W.; Alexander Bruce, 10, Portland Terrace, Plumstead, S.E.; Fred Carrodus, Glen Fern Tower, Lansdowne Road, Wimbledon, S.W.; James Codrington Crocker, 2, Flymore Villas, Swansea; Gilbert Gunn, 209, Rochdale Road, Bury, Lancs.; Frank Eustace King, Woodbury, Polworth Road, Streatham, S.W.; A. Lionel Landau, 20, Highbury New Park, N.; Charles Henry Lockitt, 5, Harley Road, S. Hampstead, N.W.; Walter Ramshaw, 5, Fronwen Terrace, Brecon; William Scholes, 151, Ainsworth Road, Radcliffe, Lancs.; Arthur Lea Butler Tindall, 41, Sunnyside Road, Ilford; Edward John Wilkinson, 8, Blenheim Terrace, Leeds; Thomas A. Young, 318, Chetham Hill Road, Manchester; Cecil Revis, 77, King Street West, Hammersmith, W.

Of the following papers, those marked * were read:—

*10. "Conversion of 1-Hydroxycamphene into β -Halogen Derivatives of Camphor." By M. O. FORSTER.

β -Bromocamphor, obtained by the action of bromine on 1-hydroxycamphene (*Proc.*, 1901, xvii., 245), yields camphor when reduced with zinc dust and acetic acid, and is hydrolysed by alcoholic potash, forming α -campholenic acid. The oxime remains indifferent to alcoholic potash, and is not converted into a nitrile under the influence of mineral acids; it yields a benzoyl derivative which crystallises from alcohol in silky needles melting at 71–73°.

β -Chlorocamphor, $C_{10}H_{15}OCl$, prepared from 1-hydroxycamphene and chlorine in acetic acid containing sodium acetate, crystallises from alcohol in long, slender prisms melting at 132.5: it has $[\alpha]_D = +39.5^\circ$ in chloroform, and $[\alpha]_D = +40.7^\circ$ in alcohol. The oxime is isomorphous with β -bromocamphoroxime, and melts at 134°; the benzoyl derivative crystallises in silky needles melting at 86°.

β -Chloro- α -bromocamphor, $C_{10}H_{14}OClBr$, produced by the action of bromine on β -chlorocamphor, crystallises from petroleum in tabular aggregates of white prisms, and melts at 101°; it has $[\alpha]_D = +126.5^\circ$ in chloroform.

The methyl ether of 1-hydroxycamphene, $C_{10}H_{15}OCH_3$, formed when the hydroxy-compound is heated with methyl iodide and dry silver oxide, is a colourless, limpid oil which boils at 193–194°, has sp. gr. 0.9314 at 20°, and $[\alpha]_D = -27.3^\circ$. The ethyl ether, $C_{10}H_{15}OC_2H_5$, resembles the lower homologue, and boils at 203–204°; bromine converts it into β -bromocamphor.

*11. "The Influence of Temperature on Association in Benzene Solution and the Value of the Molecular Rise of Boiling-point for Benzene at Different Temperatures." By W. R. INNES, M.Sc., Ph.D.

The molecular rise of boiling-point at different temperatures was determined by introducing phenanthrene, benzophenone, and benzil into benzene, boiling under reduced, atmospheric, and increased pressure. A constant pressure was maintained during each series of experiments at reduced or increased pressure by means of an automatic electrically controlled regulator. The molecular rise of boiling-point (τ) was also calculated (a) from the heat of vaporisation by means of van't Hoff's formula $100\tau = RT^2/L$ (calculated A) and (b) from the rate of change of vapour pressure with temperature by means of the equation $100\tau = Mp \left| \frac{dp}{dt} \right|$ in which M is the molecular

weight of benzene and p the mean pressure (calculated B). The calculated molecular rise and the mean experimental values found for concentrations up to 6/100 grm.-molecules per 100 grms. benzene are given in Table I.:

TABLE I.

Temperature.	54°.	58°.	63°.	73°.	80°.	93°.
Calculated A ..	21.6	22.2	23.0	25.0	26.5	29.5
Calculated B ..	21.05	21.6	22.4	24.25	25.5	27.8
Phenanthrene ..	21.0	—	22.4	23.55	25.25	27.3
Benzophenone ..	20.17	—	21.6	23.0	23.8	26.2
Benzil	—	21.0	—	—	23.3	26.24

The molecular rise calculated from the heat of vaporisation is greater than that calculated from the vapour pressure, the difference increasing with increase of temperature. The values found, using phenanthrene as the dissolved substance, agree very closely with those calculated from the rate of change of vapour pressure. The closely related substances benzophenone and benzil give numbers for the molecular rise which are almost identical. The molecular rise for benzophenone is about 0.8 less than that for phenanthrene at the same temperatures.

Series of determinations were carried out at different temperatures with the abnormal substances benzoic acid, *o*-bromobenzoic acid, β -benzil monoxime, and dimethyl tartrate. It was found that the dissociation of the complex molecules increased with the temperature between 54° and 80° in every case. Between 80° and 93° there was an apparent decrease of dissociation at all concentrations with benzoic acid and β -benzil monoxime; *o*-bromobenzoic acid and dimethyl tartrate were more dissociated at 93° in dilute solutions, but in more concentrated solutions the molecular weights became equal to those at 80° with the former substance and greater with the latter.

The heats of dissociation (Q grm. calories) of β -benzil monoxime, *o*-bromobenzoic acid, and benzoic acid were calculated from the molecular weights at different temperatures and found to be of the same order as those of a number of typical dissociating gases. Table II. gives the values calculated; V is the volume in litres occupied by the benzene in which 1 grm.-molecule of the substance, calculated as double molecules, is dissolved:—

TABLE II.

Substance.	T ₁ .	T ₂ .	V.	Q.
β -Benzil monoxime ..	278	331	13	14600
"	331	353	14	19900
<i>o</i> -Bromobenzoic acid ..	331	353	8.18	7500
"	331	353	12.3	5300
Benzoic acid	336	353	8.18	22800

The heat of dissociation of nitrogen tetroxide is 28900 cal., iodine vapour 28500 cal., acetic acid 20000 cal., and dimethyl ether hydrochloride 8600 cal.

DISCUSSION.

In reply to questions by Dr. TRAVERS, Dr. INNES said that several series of determinations of the molecular rise of boiling-point were made; there was very satisfactory agreement in every case. The series with abnormal substances at 93° was not repeated, but the fact that the molecular weight of all four substances was higher than might have been expected seemed to show that the anomalous results at this temperature are not due to ordinary experimental error, whilst from the values obtained for the molecular rise of boiling-point it appears that they are not due to a constant error in the method.

*12. "The Magnetic Rotation of Ring Compounds; Camphor, Limonene, Carvene, Pinene, and some of their Derivatives." By W. H. PERKIN, sen., Ph.D., F.R.S.

The remarkable differences between the magnetic rotations of saturated closed chain or ring compounds, such as the derivatives of tri-, tetra-, penta-, and hexa-methylene, and the open chain compounds of the aliphatic series, both unsaturated and saturated, were first referred to, the ring compounds having a much lower rotation than those which have unsaturated open chains, but the same composition; their rotation is also smaller than that of the saturated open chain compounds from which they differ in composition by $-H_2$.

On comparing the magnetic rotation of the mono- and di-carboxylic acids and ketones of the closed chain compounds with those of the corresponding saturated open chain aliphatic compounds containing the same number of carbon atoms, considerable discrepancies were observed in the amounts by which they differ from each other, which range from about 0.33 to 0.64, and this want of accord has hitherto been an enigma, but it is now found that this is due to the comparisons having been made between the wrong members of the two series. If tri-, tetra-, penta-, and hexa-methylene be taken as the first, second, third, and fourth members of the series, as they undoubtedly are, and are compared with the first, second, third, and fourth members of the aliphatic series, allowing for the difference of composition, $(CH_2)_3$, these discrepancies disappear. The differences between the rotations of these series are then found to be nearly uniform, and amount to about -0.60 in the mono- and di-carboxylic acids, ketones, and mono-chloro-derivatives of hexa-methylene. In the ring hydrocarbons, this difference is, however, much larger, amounting to about 0.988.

The next point considered was the influence of the double or bridged ring formation, in which the ring formation from the open chain compound has taken place twice, and therefore with a loss of four atoms of hydrogen. Camphor is a compound of this class, and it was found in its case that the bridged ring affected the rotation to the extent of -1.290, or a little more than twice that of the single ring. In borneol, an analogous result was obtained, whilst menthol, which contains only a single ring, gave an amount analogous to the synthetical ring compounds.

Camphene also contains a bridged ring, which is unsaturated, and after allowing for this, it gives a difference of -1.337, which is not very different from that of camphor. The magnetic rotation of pinene, which is isomeric with camphene but differs from it somewhat in the character of the bridged ring, gave results very similar to those of the latter, but which are a little higher.

In the case of the limonenes, which also are isomeric with camphene but contain only a single unsaturated ring along with the unsaturated group $CH_3 \cdot C : CH_2$ outside the ring, the rotations are very different, the value of the single ring formation, allowing for unsaturation, being practically the same as in hexamethylene, 0.988.

The rotations of chlorine and bromine derivatives of camphor and the relationships of nitro- and pseudonitro-camphor and camphoryloxime were considered, as well as

the rotation of camphylamine, bornyl chloride, or pinene hydrochloride, and dipentene dihydrochloride.

The refraction values of borneol and camphor and its derivatives were also given.

*13. "The Transport Number of very Dilute Solutions." By B. D. STEELE, B.Sc., and R. B. DENISON, B.Sc.

The object of this research was to see if it were possible to obtain by the investigation of sufficiently dilute solutions a value for the transport number for solutions of salts, such as calcium chloride, which would result in a constant specific ionic velocity when calculated from different salts of the same cation, thus bringing these salts into line with others, such as potassium chloride, to the ions of which definite specific velocities can be assigned. In order to test this question, it was first necessary to develop a method by means of which the transport number could be determined for very dilute solutions. The method employed is a simple modification of that originally used by Hittorf and lately modified by Noyes; it permits of the electrolysis of a practically unlimited volume of solution being carried out in a vessel of reasonable size.

Measurements have been made for calcium chloride, nitrate, and sulphate, and for potassium chloride, in concentrations of 1 gm. equivalent in 250 litres; and, by combination of the transport numbers found with the conductivity at infinite dilution, identical values are obtained for the velocity of the chlorine ion from solutions of the calcium and potassium salts, and for the calcium ion from solutions of the chloride and nitrate. The velocity of the calcium ion calculated from measurements of calcium sulphate solution is, however, about 3.5 per cent higher. The transport number of potassium chloride agrees with the best determinations made in solutions up to 1/10 normal, and confirms Kohlrausch's assumption that this remains constant with further dilution.

*14. "An Investigation into the Composition of Brittle Platinum." By W. N. HARTLEY, D.Sc., F.R.S.

Having had to report upon the composition of brittle platinum in the form of fragments of pins used for dental purposes, their average weight being under 20 milligrams, each, a description was given of the method by which the absence of metallic impurities, and also of silicon, was proved spectrographically. The brittle and crystalline character of the metal was shown to be in all probability caused by minute quantities of phosphorus or carbon, and by re-melting in a lime crucible under the oxyhydrogen flame its malleability was greatly improved, thus confirming the accuracy of the conclusion arrived at.

The difficulty in deciding beyond question whether there were iron lines in the platinum, or platinum in the iron spectrum, or lines of some impurity common to both metals, was pointed out, as showing the importance for practical purposes of determination of wave-lengths made with the greatest accuracy attainable, particularly in the case of such spectra as these where large numbers of lines are so closely grouped together as to have approximately the same wave-lengths.

15. "Tetrazoline." Part II. By S. RUHEMANN and H. E. STAPLETON.

The authors find that the action of methyl iodide on tetrazoline is complicated, and they described two of the substances which are formed. One of them crystallises in dark blue needles having the formula $C_3H_9N_4I_3$, and is readily decomposed by water with separation of iodine, whilst the other forms colourless, well-developed crystals, and is an iodide of the formula $C_3H_7N_4I$, which may be transformed into the corresponding chloride and into the platinichloride, $(C_3H_7N_4)_2H_2PtCl_6$. The authors gave reasons for their view that their iodide (or the chloride) is not the salt of methyl tetrazoline; their work, however, is not yet advanced enough to fix the constitution of those two compounds, or to explain the reaction by which they are formed.

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 14th, 1902.

Mr. T. H. BLAKESLEY, Vice-President, in the Chair.

THE Officers and Council for the following year were elected as follows:—

President—Prof. S. P. Thompson, D.Sc., F.R.S.

Vice-Presidents (Members who have filled the Office of President)—Dr. J. H. Gladstone, F.R.S.; Prof. G. C. Foster, F.R.S.; Prof. W. G. Adams, M.A., F.R.S.; The Lord Kelvin, D.C.L., LL.D., F.R.S.; Prof. R. B. Clifton, M.A., F.R.S.; Prof. A. W. Reinold, M.A., F.R.S.; Prof. W. E. Ayrtton, F.R.S.; Prof. G. F. Fitzgerald, M.A., F.R.S.; Prof. A. W. Rücker, M.A., F.R.S.; Sir W. de W. Abney, R.E., K.C.B., D.C.L., F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.; Prin. Oliver J. Lodge, D.Sc., F.R.S.

Vice-Presidents—T. H. Blakesley, M.A.; Prof. J. D. Everett, D.C.L., F.R.S.; S. Lupton, M.A.; J. Walker, M.A.

Secretaries—H. M. Elder, M.A.; W. Watson, B.Sc.

Foreign Secretary—R. T. Glazebrook, D.Sc., F.R.S.

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, B.Sc.

Other Members of Council—C. Chree, D.Sc., F.R.S.; W. R. Cooper, M.A.; G. Griffith, M.A.; R. A. Lehfeldt, D.Sc.; A. W. Porter, B.Sc.; W. A. Price, M.A.; W. N. Shaw, M.A., F.R.S.; W. F. Stanley, F.G.S.; J. Swinburne; A. A. Campbell Swinton, M.Inst.C.E.

Prof. S. P. Langley and Prof. H. A. Lorentz were elected Honorary Fellows to fill the vacancies caused by the deaths of Prof. Rowland and Dr. Koenig. The President of the German Physical Society was elected an *ex-officio* Fellow of the Society.

The SECRETARY then read the PRESIDENT'S Address. It commenced by giving some particulars of the life and work of Rowland, Koenig, Langley, and Lorentz. On January 11th a telegram was sent in the name of the Society to Prof. Hittorf congratulating him upon the jubilee of his professionate. The work of translation, revision, and production of an English version of Gilbert's "De Magnete" has been completed, and a copy of the book presented to the Society by the President. The remainder of the Address dealt with the refusal of the law of this country to recognise as valid matter for the granting of letters patent anything which may have been brought before any of the learned or scientific societies. In the United States a man may appeal to the fact of his having read such a paper in proof of his subsequent claim to receive a valid patent for his invention. The law of this country works very inequitably. As examples, the invention of the microphone by the late Prof. Hughes, the President's invention of the "Astigometer," and the invention of wireless telegraphy by Prof. Lodge were given.

An Ordinary Meeting of the Society was then held, at which Mr. LITTLEWOOD exhibited an Attwood's machine.

The Society then adjourned until February 28th.

CORRESPONDENCE.

THE
VOLUMETRIC ESTIMATION OF MANGANESE.

To the Editor of the Chemical News.

SIR,—As Messrs. Ibbotson and Brearley "have never denied" the statement I made relating to the oxidation of ferrous salt by dissolved oxygen, it would appear that they must admit its truth. They have not, however, while still insisting on the use of ferrous salt, issued any caution on this head. There is no occasion to add hydrogen peroxide in large excess, and it is both unscientific and wasteful to add more reagents in any

chemical operation than are necessary. Mr. Reddrop's extreme care in this respect has been more than justified in this series of articles.

My point relating to the "important rare metals" has been misinterpreted in their letter of January 31, 1902; my meaning is not very obscure.

The point in their last paragraph is doubtless explained by the fact that they have departed from the instructions, and have used 2·27 times as much spiegel as was recommended, and, further, the conditions of the experiment they describe are never realised in practice.—I am, &c.,

HUGH RAMAGE.

Cambridge, February 11, 1902.

NOTICES OF BOOKS.

Practical Electro-Chemistry. By BERTRAM BLOUNT, F.I.C., F.C.S., Assoc.Inst.C.E., Consulting Chemist to the Crown Agents for the Colonies. Westminster: Archibald Constable and Co., Limited. New York: The Macmillan Company. 1901. Pp. 374.

THE author's intention in compiling this book was to give an account of those electro-chemical processes which have already been, or are likely in the future to be, turned to industrial use. For the sake of conciseness little or no historical matter has been included, and, for the same reason, comparisons of electro-chemical processes with chemical or metallurgical methods giving the same results have been confined to showing their relative advantages, it being assumed that the reader has a knowledge of the older processes. The author has dealt with the relation between the output of any given process and the energy necessary for its proper working in a very complete manner, as well as with the practical advantages to be gained by the use of electro-chemical processes in certain cases.

The book is divided into eight sections or chapters. After the introduction and a description of the general principles of the processes, we come to the winning and electrolytic refining of such metals as copper, lead, gold, silver, nickel, cobalt, tin, antimony, and zinc; this is followed by the winning and refining of aluminium, magnesium, and sodium in igneous solution. We may here remind our readers that all electro-chemical operations are performed either by the analytical property of electric energy when passed through an electrolyte, either aqueous or fused, or by the heat produced when a current is passed through a bad conductor which is not an electrolyte.

The electric furnace devised by Moissan is next fully described, and its various uses explained, such as the production of chromium, molybdenum, tungsten, the carbides, silicides, and carbon boride.

In Section V. we have the electro-deposition of metals, such as coppering, silver, nickel, and gold-plating, and the electro-deposition of alloys. Processes for the production of alkalis, both by using a fused and an aqueous electrolyte, command a good deal of attention; amongst other products considered being caustic potash, the chlorates, hypochlorites, and perchlorates.

Section VII. is on the electrolytic manufacture of organic compounds and fine chemicals, the purification of sugar juice, electric tanning, &c.; while in Section VIII. and last, we find the various sources of power discussed; the cheapest form of power at present is that afforded by moving water, a large steam plant using cheap coal coming next. Water power is generally most abundant where it cannot well be utilised, while steam power is uneconomical. What is really wanted is a direct method of converting the energy stored up in coal into electrical energy; this problem, however, has yet to be solved.

We must congratulate the author on the success he has achieved in turning out a really sound work, which is at the same time well and clearly printed and indexed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 4, January 27, 1902.

Certain Properties of the Radiation emitted by Radio-active Bodies.—Henri Becquerel.—The author concludes from a series of experiments that, in the radiation from uranium, either there does not exist the non-deviable and slightly penetrating portion of the radiation; or, if it does exist, it is not emitted with an intensity in proportion to the intensity of the deviable portion or of the same order of magnitude as in the case of radium radiation. A second series of experiments show that the deviable portion of the radiation of radium, identical with cathode rays, transforms white phosphorus into red. It is very probable that the very absorbable non-deviable portion might also be very active in effecting this transformation, but, on account of the necessity of preserving the radium, a glass tube has to be used to contain it, and this cuts off all the latter rays.

Vapour-tension of Hydrogen Selenide and the Dissociation of its Hydrate.—M.M. de Forcrand and Fonze-Diacon.—It is already known that the vapour-tension of hydrogen selenide is 760 m.m. at -42° . The authors now obtain other points on the curve of vapour-tension, and from these numbers are enabled to calculate the heat of volatilisation of hydrogen selenide. Six fairly concordant values were obtained whose mean is 4.74 cal. The existence of the hydrate of hydrogen selenide may be proved by filling a flask with the damp selenide and exposing it to a temperature of about $+5^{\circ}$ C. A colourless crystallised hydrate is seen, which has apparently the same stability as the hydrates of chlorine, sulphurous anhydride, and methyl chloride. The tensions of dissociation of the hydrate were measured.

Lithium Antimonide, and the Preparation of some Alloys of this Metal.—P. Lebeau.—Antimony and lithium easily combine, with evolution of a great deal of heat. The violence of the reaction prevents the possibility of practically obtaining a definite compound by direct union. On the contrary, by electrolysis a mixture of equal weights of lithium chloride and potassium chloride with a cathode of antimony, a well crystalline antimonide of lithium is produced. This substance is not easily fusible, and corresponds to the formula SbLi_3 . This same method of operation applies to the preparation of a considerable number of lithium alloys.

Action of Copper Hydrate on Aqueous Solutions of Metallic Salts.—A. Mailhe.—The author showed in two preceding papers that tetracupric hydrate gives with aqueous solutions of chlorides, bromides, and metallic sulphates mixed basic salts. This particular action of tetracupric hydrate on solutions of metallic nitrates leads, in all cases when a mixed salt is produced, to a compound of the tetra-metallic type, isomorphous (except in the case of cadmium nitrate) with tetracupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{CuO} \cdot 3\text{H}_2\text{O}$, to which type the others correspond. Pélégot's blue hydrate reacts sometimes with solutions of metallic nitrates to give a crystalline compound, but more often a less interesting amorphous body is produced.

Glyceroarsenic Acid.—V. Auger.—Arsenic acid and glycerin react very strongly on each other, producing the ether acids, setting free one or two molecules of water, but the product obtained is immediately hydrolysed in contact with the free water. This excludes the possibility of a preparation of an arsenio-glycerate by the wet method.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, February 25, Mr. W. H. Shaw, F.R.S., Secretary of the Meteorological Council, will begin a course of two lectures at the Royal Institution on "The Temperature of the Atmosphere, its Changes and their Causes"; and on Thursday, February 27, Sir Henry Craik, K.C.B., will deliver the first of two lectures on "Scotland's Contribution to the Empire." The Friday Evening Discourse on February 28 will be delivered by Professor H. A. Miers, his subject being "Gold Mining in Klondike"; and on March 7 Professor Becquerel, Membre de l'Institut, Paris, will deliver a Discourse on "Radio-Active Bodies" (in French).

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Society of Arts, 8. (Cantor Lectures). "Personal Jewellery from Prehistoric Times," by Cyril Davenport.
- TUESDAY, 25th.—Royal Institution, 3. "The Temperature of the Atmosphere—its Changes and their Causes," by W. N. Shaw, M.A., F.R.S.
- WEDNESDAY, 26th.—Society of Arts, 8. "Recent Inventions in Weaving Machinery," by Prof. Roberts Beaumont, M.I.Mech.E.
- THURSDAY, 27th.—Royal Institution, 3. "Scotland's Contribution to the Empire," by Sir Henry Craik, K.C.B.
- Society of Arts, 4.30. "The Industrial Development of India," by Nilkanth B. Wagle, B.A.
- FRIDAY, 28th.—Royal Institution, 9. "Gold Mining in Klondike," by Prof. Henry A. Miers, F.R.S., &c.
- SATURDAY, March 1st.—Royal Institution, 3. "Some Electrical Developments," by Lord Rayleigh, F.R.S., &c.

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February 4, 1902.

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THE CHEMICAL NEWS.

Vol. LXXXV., No. 2205.

THE STRATIFICATIONS OF HYDROGEN.*

By Sir WILLIAM CROOKES, F.R.S.

(Concluded from p. 87).

Stratifications in Pure Hydrogen.

THE arrangement of the apparatus is shown in Fig. 5. The three hydrogen generators are called Nos. 1, 2, and 3. In No. 1, the gas is generated by the action of hydrochloric acid on zinc. This crude hydrogen is only used to drive out the air from the rest of the apparatus, and to remove the air dissolved in the liquids. When it had done its work, the generator was sealed off between Nos. 1 and 2, at A. It was considered that having the apparatus to begin with full of even somewhat impure hydrogen was better than starting with it full of air. The second and third generators contain at the bottom a pasty amalgam

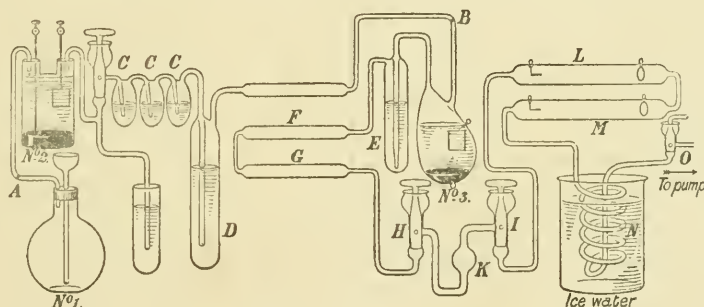


FIG. 5.

of mercury and zinc forming one pole, and a piece of platinum forming the other pole; the electrolyte is dilute hydrochloric acid. Platinum wires sealed through the sides of No. 3 carry the current from three Grove's cells to the interior. After the apparatus has had generator No. 1 removed, a large quantity of hydrogen is passed through from the second generator, with the object of replacing the impure hydrogen by some of a purer quality. When No. 2 is exhausted, it also is sealed off at B, leaving only the third generator with its drying tubes connected with the apparatus. Before sealing off No. 2, filling and exhausting is carried on until the hydrogen shows no impurity when spectroscopically examined in a capillary tube attached to the vacuum tube. The gas from the first and second generators bubbles first through strong caustic soda, C, C, C, to remove any acid carried over from the generators, then through strong sulphuric acid, D, to take away the bulk of the moisture, and thus save the drying tubes; it then passes through the purifying arrangements more especially connected with the third generator. Having sealed off Nos. 1 and 2, gas is evolved from No. 3 generator. Hence it passes through strong sulphuric acid in the tube H; then over a tube filled with granulated caustic soda, F; and next through a tube, G, tightly packed with phosphoric anhydride. H and I are two taps, having a reservoir, K, between them. When full of gas, H and I are closed, and the tubes L and M, after having been exhausted to a high point, can then be fed with limited amounts of pure dry hydrogen by slightly opening tap I, and closing it when equilibrium is restored between L,

M, and K. N is a spiral of narrow glass tubing immersed in a beaker of ice and water. At O is a tap to keep mercury from diffusing into the pump if the apparatus has to be left all night. The vacuum tube, L, is provided with aluminium poles, and the tube M has the platinum poles made double for heating purposes, as shown in Fig. 3.

Hydrogen from the first generator was passed through the apparatus for two hours, when it was sealed off. The whole apparatus was exhausted to a high point, and No. 2 generator was set to work. Hydrogen was passed several times at full pressure through the apparatus for one or two hours, and then exhausted to the stratification point. During these operations the platinum terminals of one of the vacuum tubes were heated to full redness, and the current was kept on both tubes for some hours to drive off occluded gases.

Finally the second generator was sealed off, and hydrogen used from the remaining generator. After much washing out with hydrogen at the ordinary pressure, exhaustion and re-filling were continued, and finally the reservoir K was filled, both taps, H and I, being closed. The tubes were highly exhausted to the non-conducting point, and tap I opened and then closed, so as to introduce a little hydrogen. H was then opened and again closed, so as to equalise the pressure in I, and exhaustion proceeded to the stratification point. At first the strata

were irregularly coloured with a suspicion of blue on one face, but as the operations just described were continued, the blue faces disappeared, the stratifications assumed a pure pink hue, and showed the hydrogen spectrum alone; no mercury was detected in any part of either tube.

From the first to the eighth filling the strata were pink with a trace of slaty blue colour on the faces next the negative pole. From the tenth filling the blue faces disappeared, and after the twentieth filling no trace of blue could be seen, and the spectrum of hydrogen alone was visible.

On examining the spectra of the stratified gas in the two tubes, each showed strongly the line spectrum of hydrogen; but while the spectrum in the platinum-poled tube showed pure red, blue, and green lines on a black ground, that in the aluminium-poled tube showed in addition the fainter hydrogen line spectrum in the yellow and orange. This result may be due to the greater surface exposed by the aluminium poles; it was not further examined.

Having at last succeeded in getting hydrogen free from mercury, experiments were instituted to verify the inference that the blue components of the blue and pink strata usually attributed to hydrogen were really due to the presence of a trace of mercury.

Origin of the Blue Component of Parti-coloured Stratifications.

I used an apparatus similar to the last, but with only one generator. If my idea was correct, that the mercury in the course of a few hours diffused into the hydrogen

* A Paper read before the Royal Society, February 6, 1902.

tube from the pump when it was not at work, there ought to be an access of blue faces to the pink buttons after the exhausted apparatus had been at rest. After filling with hydrogen and exhausting several times, a hydrogen vacuum was obtained showing no blue faces to the pink strata. The apparatus was then left all night, and the stratifications examined next morning. The blue colour to each face was now unmistakably visible. The refilling with hydrogen and exhausting was then continued. It was not possible in this way to get the tube entirely free from mercury, although it got less and less, as shown by the diminution of the blue faces.

Occasionally, when no mercury was present, a faint blue edging to some of the front pink strata was seen. This blue was too faint to show lines in its spectrum. After much searching the blue tint was traced to the phosphoric drying tubes. A clean tube was taken for stratifications, and sealed to the apparatus used in the last experiments. The whole was exhausted to a high point, and one of the phosphoric anhydride tubes was gently heated with a gas flame, the current kept going. Instantly a flood of blue light swept through the tube, and when concentrated in a narrow constriction the light showed a complicated spectrum which was not recognised; none of the characteristic lines of the phosphorus spectrum could be seen in it. The tube was cleared of the blue colour by introducing hydrogen and pumping it out a few times, and then hydrogen was introduced and exhaustion continued to the stratification point. The strata now were pink with no appearance of blue. Warming the phosphoric anhydride tube at once reproduced the faint blue edging to the pink discs. This blue colour was different both in tint and intensity to the blue colour produced by mercury, but it was too faint to show a spectrum except in the constricted part.

It is of importance to ascertain whether the body producing this blue colour can be removed from the phosphoric anhydride. The drying tube was again heated to the subliming point of the anhydride, hydrogen passed in, and the pump worked until the vacuum was almost non-conducting. The heating, passing in hydrogen, and pumping were several times repeated, the impurities diminishing each time. Ultimately a point was reached when, the tube being non-conducting, heating the phosphoric anhydride did not communicate any gas to the vacuum tube. At this stage the phosphoric anhydride still retained unimpaired its affinity for water. In any accurate experiment, therefore, the phosphoric anhydride tubes should have a preliminary heating in a vacuum to eliminate the impurity. This may be done with several tubes at a time, when they can be sealed at each end and preserved for future use.

It is thus seen that this blue glow is due to some impurity in the phosphoric anhydride. Likewise I have shown from the examination of its spectrum that it is not due to phosphorus. The glow probably is due to some intermediate oxide of phosphorus. In any accurate work with the mercury pump, where phosphoric anhydride is used as the drying agent, this source of impurity must not be overlooked.

An addition to the apparatus was made, a supplementary tube sealed on containing a grain of corrosive sublimate. This was used as being non-volatile at the ordinary temperature, but easily vaporised by heat. The experiment last described was continued, and immediately after the phosphoric blue edge appeared fresh hydrogen was let in and exhaustion continued till the faint blue was eliminated. The mercury salt was then heated, when immediately a rich blue edging appeared on the face of each pink stratification and the yellow lines of mercury shone out distinctly. Mercury blue is of a fuller colour than that of the phosphoric blue.

Altering the Colour of Stratifications.

In the *British Association Reports* for 1865 (Abstracts, p. 15), Mr. Cassiot describes the changes produced in the

colours of the stratifications by introducing a water resistance in series with the vacuum tube. Having shown that the blue components of the stratifications are due to the presence of a trace of mercury with the hydrogen, experiments were commenced to ascertain what difference in the strength of the induced current would be necessary to alter the relative intensities of the pink and blue strata. Accordingly, I fitted up a resistance, shown in Fig. 6,

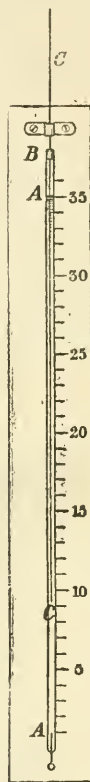


FIG. 6.

consisting of a glass tube, A, 3 feet long and $\frac{3}{8}$ inch diameter, nearly filled with distilled water. Through a cork, B, at the upper end of the tube a copper wire, C, passes, and by raising or lowering the wire either the whole resistance of the water or any fraction of it can be thrown into the circuit. The upper part of the wire is connected with one pole of the coil and the water is connected with the other pole by means of a small platinum wire sealed through the bottom of the tube.

The wire was pushed down until it touched the platinum at the bottom, thus cutting out the water resistance. The strength of hammer-spring and the exhaustion were arranged to show good pink and blue discs. The wire was then gradually withdrawn, when the blue components gradually faded, and at a resistance of 6 inches of water the stratifications were all pink. Spectroscopic examination showed that in the parti-coloured state mercury was strongly present in all the blue components, together with the C hydrogen line; the mercury spectrum, however, being in excess. But when the water resistance was put in, and the buttons were all pink, mercury was still to be detected, but the hydrogen spectrum was more prominent. The green line of mercury was always the first to appear, and when the hydrogen became visible the first line to appear was the red.

That the change from parti-coloured stratifications to all pink is occasioned by an alteration in the intensity of the spark, is also shown by the fact that altering the make and break of the coil produces the same change as putting in the water resistance. Screwing up the hammer-spring so as to induce strong magnetism in the core and high potential of spark, gives pink and blue parti-coloured buttons. Weakening the spring, and thus weakening the magnetism, gives buttons which are all pink. I cannot, however, in this way cause the migration of the blue buttons to one single button in front. This phenomenon is produced only by an alteration of the exhaustion. Conversely, an alteration of the exhaustion will not change parti-coloured buttons to buttons of all one colour; this requires a change in electrical energy.

I consider the water resistance acts thus:—At the same rarefaction, hydrogen conducts the current better than mercury vapour. With a strong induction-spark at a certain degree of exhaustion, the conducting power of the rarefied hydrogen is not sufficient to carry the whole of the current; some of it, therefore, is conducted through the mercury vapour, when the intensity of the blue drowns the feebler colour of the hydrogen. When, however, a resistance of 6 inches of water (equal to about 500,000 ohms) is inserted, the current is so weakened that the hydrogen can carry the whole of it, and the blue of the mercury is not seen.

Conclusions; Chiefly Theoretical.

The phenomenon of blue faces on the pink discs is probably due to some such action as the following:—At the exhaustion necessary to give stratifications, there is a wide dark space round the negative pole. Here the

negative electrons (Radiant Matter), issuing from the pole with enormous velocity, have sufficient energy to clear a space in front of them to a distance varying with the degree of exhaustion.

Dr. A. Schuster considers that the discharge through mercury vapour in a vacuum tube, when quite free from air, will not give rise to stratifications, nor to the dark negative space (Dr. A. Schuster, "Experiments on the Discharge of Electricity through Gases," *Roy. Soc. Proc.*, vol. xxxvii., p. 318). My own experiments (*Journ. of the Inst. Electrical Engineers*, vol. xx., p. 44) show that the dark space will form in pure mercury vapour. Whichever view may be correct, there is no doubt that if stratifications in mercury vapour are not altogether unknown, they are much more difficult to produce than similar phenomena in hydrogen or other diatomic gases. At a certain critical stage of the exhaustion, when both hydrogen and mercury are present, I obtain both mercury and hydrogen strata.

The following experiments appear to show that the presence of hydrogen* has a considerable influence on the behaviour of mercury vapour in vacuum tubes. A tube with aluminium terminals had been attached to the pump for several days, and consequently mercury had diffused in and condensed on its sides. The tube was exhausted until, under the electric discharge, it phosphoresced of a brilliant green and was near the non-conducting point. It was heated very strongly with a Bunsen flame, when a faint pink luminosity was observed between the poles, the spectrum of mercury being absent. The tube was allowed to cool and a little hydrogen was introduced, when the usual pink stratifications appeared. On heating the tube to about the same temperature as before blue faces showed on the pink buttons, and the mercury spectrum was seen throughout the tube, especially in the neighbourhood of the negative pole.

It is known that in a vacuum tube, at an exhaustion approaching the stratification point, any slight obstruction, such as constriction in the tube, or a series of wires sealed in, will cause luminous strata to hang round the obstruction. In a similar way, the hydrogen strata afford an anchorage, as it were, for the mercury, each hydrogen luminosity having a little blue glow of mercury hanging on to it; whereas, were there no hydrogen, no mercury stratifications would be seen.

The pink and blue luminosities show where the electrons and gaseous atoms meet; when the speed of the electrons is suddenly diminished, the shock throws the atom into greater vibration, which, being communicated to the ether, produces vibrations of definite wave-lengths, constituting the special spectrum of the atom. The dense mercury atom is not driven back so much as the lighter hydrogen atom—hence the blue front to the pink buttons. A very little difference in the exhaustion suffices to break the adhesion between the mercury and the hydrogen; then the mercury vapour diffusing along the tube meets the electrons from the negative pole and is swept back to the head of the hydrogen strata, and becomes apparent as a single button of blue light.

Radiant Matter. Electrons.

I have spoken of "Radiant Matter" and "Electrons" as if they were identical. Nearly twenty-five years ago I was led by experiments in highly rarefied tubes to assume the existence of matter in an *ultra-gaseous* state. Later, in a lecture delivered before the British Association at the Sheffield Meeting, 1879 (*CHEMICAL NEWS*, vol. xl., pp. 91, 104, 127), I first used the expression "Radiant Matter," or matter in the *ultra-gaseous* state, to explain the novel phenomena of phosphorescence, trajectory, shadows, mechanical action, magnetisation, and intense heat. "In studying this fourth state of matter," I said, "we seem at length to have within our grasp and obedient to our con-

trol, the little indivisible particles which with good warrant are supposed to constitute the physical basis of the universe. We have seen that in some of its properties radiant matter is as material as this table, whilst in other properties it almost assumes the character of radiant energy. We have actually touched the borderland where matter and force seem to merge into one another" (*CHEMICAL NEWS*, vol. xl., p. 130).

In twenty-five years one's theories may change, although the facts on which they are based remain immovable. What I then called "Radiant Matter" now passes as "Electrons," a term coined by Dr. Johnstone Stoney, to represent the separate units of electricity, which is as atomic as matter. What was puzzling and unexplained on the "Radiant Matter" theory is now precise and luminous on the "Electron" theory. Thus my early hypotheses fall into order by the substitution of one expression for the other. A chemical ion consists of a material nucleus or atom of matter constituting by far the larger portion of the mass, and a few electrons or atoms of electricity. The electrons are the same as the "satellites" of Lord Kelvin and the "corpuscles" or "particles" of J. J. Thomson.

Electrons probably leave the negative pole with a velocity nearly uniform, modified to a considerable extent by the degree of exhaustion, and to a less extent by the electromotive force behind them. Many experiments—the details I must leave to a future occasion—show that the liberated electrons do not behave as a gas, *i.e.*, they have not properties dependent on inter-collisions, mean free path, &c.; they act more like a fog or mist, are mobile, and carried about by a current of air to which they give temporary conducting powers, clinging to positively electrified bodies and thereby losing mobility, and settling on the walls of the containing vessel if left quiet.

On the other hand, the crowd of hydrogen or mercury atoms, by virtue of molecular motion and inter-collisions, act as gases. Whilst their *mean* free paths are conditioned by the degree of exhaustion, there may be amongst them a certain number of *actual* free paths differing widely on each side of the mean. Under the influence of the electromotive force, and at the right degree of exhaustion, these atoms arrange themselves in groups (see Note A), while the rushing swarm of electrons driven from the negative pole meet them and render them visible. According to J. J. Thomson the mass of an electron is about the 1/700th part of that of the hydrogen atom, and as these masses start from the negative pole in a vacuum tube with a velocity of the order of half that of light, it is easy to see that their heating, phosphorescent, and mechanical power must be stupendous.

The basis of the Electron, as I foreshadowed in 1879 in the case of Radiant Matter, is probably the same in all cases—the Protyle from which the chemical atoms were assumed to be formed (*Report of the Fifty-sixth Meeting of the British Association*, Birmingham, 1886, p. 568, Address to the Chemical Section).

On the two-fluid theory, the electrons constitute free negative electricity, and the rest of the chemical atom is charged positively, although a free positive electron is not known. It seems to me simpler to use the original one-fluid theory of Franklin, and to say that the electron is the atom or unit of electricity (see Note B). Then a so-called negatively charged chemical atom is one having a surplus of electrons, the number depending on the valency, whilst a positively charged atom is one having a deficiency of electrons. Differences of electrical charge may thus be likened to debits and credits in one's banking account, the electrons acting as current coin of the realm.

Notes.

A. In an Address delivered before the Institution of Electrical Engineers, January 15th, 1891, I gave an outline of a theory of stratifications in rarefied gases. The following quotation renders my meaning clear:—"If, in any much frequented street, at some time when the stream of

* Possibly another gas would do as well. Hydrogen was used because in this instance the hydrogen generator was attached to the tube.

traffic runs almost equally in both directions, we take our stand at a window from which we can overlook the passing crowd, we shall notice that the throng on the footway is not uniformly distributed, but is made up of knots—we might almost say blocks—interrupted by spaces which are comparatively open, we may easily conceive in what manner these knots or groups are formed: some few persons walking rather more slowly than the average rate slightly retard the movements of others, whether travelling in the same or in an opposite direction. Thus a temporary obstruction is created. The passengers behind catch up to the block and increase it, and those in front, passing on unchecked at their former rate, leave a comparatively vacant space. If a crowd is moving all in the same direction, the formation of these groups becomes more distinct. Hence mere differences in speed suffice to resolve a multitude of passengers into alternating gaps and knots. Instead of observing moving men and women, suppose we experiment on little particles of some substance, such as sand. If we mix the particles with water in a horizontal tube and set them in rhythmical agitation, we shall see very similar results, the powder sorting itself with regularity into alternate heaps and blank spaces. If we pass to yet more minute substances, we observe the behaviour of the molecules of a rarefied gas when submitted to an induction current. The molecules here are free, of course, from any caprice, and simply follow the law I seek to illustrate, and though originally in a state of rampant disorder, yet under the influence of the electric rhythm, they arrange themselves into well-defined groups or stratifications."—*Fourn. of the Inst. Elect. Engineers*, vol. xx, p. 10.

B. "The theory of definite electrolytical or electrochemical action appears to me to touch immediately upon the *absolute quantity* of electricity or electric power belonging to different bodies. . . . And when comes the fact that the electricity which we appear to be capable of loosening from its habitation for a while, and conveying from place to place, *whilst it retains its chemical force*, can be measured out, and being so measured, is found to be *as definite in its action* as any of those portions which, remaining associated with the particles of matter, give them their *chemical relation*; we seem to have found the link which connects the proportion of that we have evolved to the proportion of that belonging to the particles in their natural state."—Faraday's "Experimental Researches in Electricity," par. 852.

"The equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity; . . . it being the ELECTRICITY which determines the equivalent number, *because* it determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalents to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them."—*Ibid.*, par. 869.

"In former investigations of the action of electricity it was shown . . . that the quantity of electric power transferred onwards was in proportion to, and was definite for, a given quantity of matter moving as anion or cation onwards in the electrolytic line of action; and there was strong reason to believe that each of the particles of matter then dealt with, had associated with it a definite amount of electrical force, constituting its force of chemical affinity."—*Ibid.*, par. 1707.

(In all the above quotations the italics and capitals are Faraday's).

"It is therefore extremely natural to suppose that . . . every molecule of the cation is charged with a certain fixed quantity of positive electricity, which is the same for the molecules of all cations, and that every molecule of the anion is charged with an equal quantity of negative electricity."—Clerk Maxwell's "Treatise on Electricity and Magnetism," first edition, vol. i., 1873, p. 308.

"This definite quantity of electricity we shall call the

molecular charge. If it were known, it would be the most natural unit of electricity."—*Ibid.*, p. 311.

"Suppose . . . we call this constant molecular charge, for convenience in description, *one molecule of electricity*."—*Ibid.*, p. 312. (The italics are Maxwell's).

"Nature presents us with a single definite quantity of electricity. . . . For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte, which is the same in all cases."—G. Johnstone Stoney, "On the Physical Units of Nature," British Association Meeting, 1874, Section A; *Phil. Mag.*, May, 1881.

"The same definite quantity of either positive or negative electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion."—Helmholtz, Faraday Lecture, 1881.

"Every monad atom has associated with it a certain definite quantity of electricity; every dyad has twice this quantity associated with it; every triad three times as much, and so on."—O. Lodge, "On Electrolysis," *British Association Report*, 1885.

ON RADIO-ACTIVE THORIUM.*

By K. A. HOFMANN and F. ZERBAN.

ACCORDING to the experiments of G. C. Schmidt, preparations of thorium possess the property of radio-activity. Rutherford has devised further methods of investigating this subject, and Debiere has then isolated from pitchblende a substance which was very strongly radio-active, and which behaved chemically like thorium. Since now the mineral bröggerite, which is rich in thorium, is related to pitchblende, it was to be conjectured that from bröggerite active thorium could be obtained in greater quantity than was possible from pitchblende. K. A. Hofmann and E. Strauss established the fact that the thorium ore isolated from bröggerite by the usual methods produced a strong effect on photographic plates. The thorium from cleveite and samarskite was also radio-active.

We have pursued these investigations and have found that the activity of the preparations of thorium from the above named minerals may be considerably augmented by fractional precipitation with concentrated solution of potassium sulphate, with potassium chromate, hydrogen peroxide, and sodium thiosulphate, by which means the activity is concentrated into those portions which are precipitated most readily.

On the other hand, on treatment with ammonium carbonate the active substance passes over into the more soluble fractions. Thus we hoped to be able to isolate the radio-active substance by repeated fractionation. But to our great surprise we found that, after keeping our preparation (as oxide in closed preparation tubes) for five months, its activity had very greatly diminished. For example, in June last year the most active thorium oxide from bröggerite, cleveite, and samarskite strongly blackened the photographic plate through glass, while in the following November the same substances, examined in the same way, produced only weak, and, in some cases, no perceptible effects. At the present time, *i.e.*, in January, none of these preparations produces any effect in ten hours through glass on the photographic plate, and most of them produce no effect through thin aluminium leaf. The decrease of activity may be conclusively proved by means of the electroscope.

Thus a bröggerite preparation, which was strongly active in June, discharged the electroscope in November in 1 min. 0 sec., while the electroscope without any radio-active substance lost its charge in 4 mins. 40 secs. The corresponding numbers in January were 3 mins. 45 secs. and 3 mins. 50 secs. Another bröggerite preparation

* Communication from the Chemical Laboratory of the Royal Academy of Science at Munich.

discharged in November in 1 min. 50 secs. (electroscope without radio-active substance, 4 mins. 40 secs.); in January in 2 mins. 30 secs. (electroscope without substance, 2 mins. 55 secs.). A clèveite preparation in November in 1 min. 10 secs. (electroscope without radio-active substance, 4 mins. 40 secs.); in January in 2 mins. 5 secs. (electroscope without radio-active substance, 2 mins. 15 secs.). A preparation from samarskite in November in 1 min. 30 secs. (electroscope without radio-active substance, 4 mins. 40 secs.); in January in 1 min. 50 secs. (electroscope without radio-active substance, 2 mins. 15 secs.). Another preparation from the same mineral in November in 3 mins. 45 secs. (electroscope without radio-active substance 4 mins. 50 secs.); in January in 3 mins. 40 secs. (electroscope without radio-active substance, 3 mins. 40 secs.).

According to these results we must assume that the thorium from bröggerite, clèveite, and samarskite possesses no primary, but only an induced activity. The supposition that the uranium always present in the minerals mentioned has exercised the original inductive action on the thorium has been confirmed. For we found that thorium preparations from a Brazilian monazite sand free from uranium were absolutely inactive immediately after their separation, both as regards the photographic plate, through thin aluminium leaf, through glass, and through caoutchouc, and also as regards the electroscope. This monazite sand contains no trace of uranium, but the thorium ore prepared from it became very strongly active after we had left it for a long time in contact with feebly active uranium. In order to meet the objection that the uranium employed by us contained another radio-active substance which mixed with the thorium during our experiment, the middle fraction, obtained by fractional crystallisation of the bröggerite-uranium as double salt with ammonium oxalate, was purified from all substances which are active in the above sense, by means of sulphuretted hydrogen, then with sulphuric acid, and finally with oxalic acid. The uranium thus obtained, when ignited to U_3O_8 , showed itself feebly active.

Five grms. of this uranic-uranous oxide were ground fine together with 1 grm. of thorium from monazite sand, the mixture heated for four hours to 400° , and after cooling in a small closed preparation tube, left for fourteen days. Then it was dissolved by means of nitric acid, the thorium precipitated with oxalic acid, and ignited after careful washing. A similar experiment was performed with thorium from bröggerite, which had once been strongly active, but had become inactive through long keeping. Both thorium preparations now showed themselves to be strongly active, and even after four weeks they discharged the electroscope in 1 min. 5 secs. and 1 min. 15 secs. (electroscope without radio-active substance, 4 min. 0 sec.).

The uranium obtained from the filtrates of both thorium oxalates, when ignited to U_3O_8 , appeared more feebly active than before. This result agrees with that of Becquerel, who showed that, by repeated addition of barium chloride and repeated precipitation with sulphuric acid, almost inactive uranium preparations may be obtained from the active uranium salt, while the precipitates of barium sulphate are active.

Our supposition that the activity of the thorium preparation from the minerals examined by us, i.e., bröggerite, clèveite, and samarskite, is dependent on the presence of uranium, has been confirmed by the examination of other thorium minerals as well as by the above mentioned experiments. Bröggerite and clèveite contain a great deal of uranium (about 78 per cent U_3O_8), and strongly active thorium. Considerably less uranium occurs in samarskite (about 4 per cent U_3O_8), and the thorium ore obtained from it is correspondingly less active. Thorite with 50 per cent thorium and 10 per cent uranium is feebly active, orangite with 70 per cent thorium and 1 per cent uranium still more feebly active, and Brazilian monazite sand (free from uranium) is an inactive thorium preparation.—*Berichte der Deutschen Chem. Gesell.*, February, 1902.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART XII.

By HARRY BREARLEY.

(Continued from p. 89).

IRON.

JOURNALS to end of 1900. The classification is—

- I. SEPARATIONS FROM OTHER METALS.
- II. GRAVIMETRIC ESTIMATIONS.
- III. VOLUMETRIC ESTIMATIONS.
 - a. As Ferrous Salts.
 - b. As Ferric Salts.
- IV. COLORIMETRIC ESTIMATIONS.
- V. MISCELLANEOUS.

I. SEPARATIONS FROM OTHER METALS.

Lime and Magnesia.—

1635. ROSE (C. N., ii., 291).—Add $AmHO$; any $CaCO_3$ formed is decomposed on boiling if $AmHO$ salts are present.
1636. CALVERT (C. N., ii., 328).— CaO is not separated with $AmHO$. Precipitate neutralised iron solution as basic succinate.
1637. GIBBS (C. N., xi., 102).—Fe and Al are separated as acetate from Ca, Mg, Zn, and Ur.
1638. GUYARD (C. N., xlix., 259).—Keeping Fe, Al, &c., in solution as citrate, Ca may be precipitated as oxalate and Mg as phosphate.

Uranium (see also 1637).—

1639. PISANI (C. N., iii., 257).—Precipitate Fe with Am_2CO_3 and separate the little Fe in the filtrate with Am_2S .
1640. BURKER (C. N., xxxviii., 276).—Process 1639 inaccurate. Precipitate with $AmHO$, weigh, reduce in H, and dissolve out the Fe with HCl (see 961).
1641. WALKER (J. C. S., lxxiv., ii., 540).—Pour acid mixture into $NaHO + H_2O_2$; U in the filtrate. RHEINECK (C. N., xxiv., 233).—Proceeds as 1637.
1642. CLASSEN (J. C. S., xlviii., 192).—Fe deposited from solution containing large excess of oxalate leaves U in solution.

Beryllium.—

1643. SCHLEIER (J. S. C. I., 1892, 713) and ATKINSON and SMITH (J. C. S., lxx., ii., 220).—Fe precipitated with nitroso- β -naphthol.
1644. HAVENS and WAY (C. N., lxxx., 285).—Be, Cr, and Zr are separated as in 1410).

Arsenic.—

1645. JANNASCH and KAMMERER (J. C. S., lxx., ii., 221).—Pour HCl solution into $NaHO + H_2O_2$; As in solution.

Cadmium.—

1646. STORTENBECKER (C. N., lxxx., 16).—The Fe is converted to ferrocyanide and the Cd electro-deposited.

Zirconium.

1647. MATTHEWS (C. N., lxxix., 97).—Method based on insolubility of oxychloride of Zr, &c., in ether. Ce, Ti, &c., are similarly separated. Résumé of methods for separating Fe and Zr.

Thallium.—

1648. CROOKES (C. N., vii., 194).—Reduce to FeO with hypo. and precipitate Tl with KI . Indicates 0.0002 grm.

Cerium (see also 1647).—

1649. GIBBS (C. N., x., 195).—Add saturated Na_2SO_4 . Ce, La, Dy are precipitated; Fe, Al, Gl, Yt, and Ur are in solution.

II. GRAVIMETRIC ESTIMATIONS.

1650. FRESSENIUS (C. N., iv., 150).— Am_2S precipitates Fe slowly, but completely; AmCl assists; AmHO not harmful; ferric salts imperfectly precipitated.
1651. BLUM (Z. S. C. I., 1888, 456).—Mix with tartaric acid, precipitate with Am_2S , dissolve in HCl , precipitate with AmHO , and weigh as Fe_2O_3 .
1652. KONINCK (C. N., lxii., 19) and MEINECKE (Z. S. C. I., 1888, 237).—Precipitate neutralised solution with nitroso- β -naphthol and ignite to Fe_2O_3 . Al is separated, but not Cu, Co, and P.
1653. CROSS (C. N., xxxvii., 26).—Extent of error introduced by precipitating $\text{Fe}_2(\text{HO})_6$ in the presence of salts of the alkalis and alkaline earths.
1654. MEUNIER (C. N., xx., 264).—Powdered meteoric stones digested with AuCl_3 . Amount of Au deposited is estimated.
1655. KRUG (C. N., lxxv., 69).—Résumé of methods for estimation of Fe (and Al) in the presence of P_2O_5 . The following refer mainly to the valuation of agricultural products:—OGILVIE (C. N., xxv., 277); DYER (C. N., liii., 51); JONES (C. N., liii., 87; and lxxv., 234); MELLON (C. N., liii., 85); GLASER (C. N., lxi., 181); GRÜBER (C. N., lxxiii., 146); PELLET (C. N., xxxv., 268); VINCENT (C. N., lxx., 297); GLADDING (C. N., lxxiv., 112 and 146); BLATTNER and BRASSEUR (C. N., lxxvi., 150); LINDET (C. N., lxxvi., 212); and many others.

The following refer to electrolytic depositions:—

1656. SMITH (Z. S. C. I., 1888, 693). Al and Ti do not interfere; BRAND (Z. S. C. I., 1889, 1011); RUDORFF (Z. C. S., lxiv., ii., 93); HEIDENREICH (Z. S. C. I., 1896, 744); NICHOLSON and AVERY (C. N., lxxiv., 91); and AVERY and DALES (Z. S. C. I., 1899, 300 and 610).

III. VOLUMETRIC ESTIMATIONS.

a. As Ferrous Salts.—

1657. BLUNT (C. N., viii., 54).—Very dilute solutions of HCl decompose permanganate. Rate of decoloration observed.
1658. ZIMMERMAN (C. N., xlvii., 12).—Presence of MnO salts prevents perturbing action of HCl in KMnO_4 titrations. See also KRUTWIG (C. N., xlviii., 102); THOMAS (C. N., xlviii., 119) uses lead chloride for the same purpose; HOOD (C. N., l., 278) uses MgSO_4 or Am_2SO_4 ; LUKE (C. N., lviii., 186), sulphates of Ca, Co, and Mg have no value in this respect (see 1676).
1659. MOYANCE (C. N., xx., 45).—Reduction to FeO best effected by amalgamated Zn. Best means of making KMnO_4 estimation stated.
1660. KOPP (C. N., xxix., 242).—Uses SnCl_2 to accelerate the reduction by Zn.
1661. BEEBE (C. N., liii., 269).—Suspends the amalgamated Zn in a Pt basket.
1662. DONATH and JELLER (C. N., liv., 73).—Mix ignited $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ with Zn powder, heat, dissolve iron in H_2SO_4 , and titrate. Process separates Fe from Al and Cr. JUPTNER (Z. I. S. I., 1894, ii., 497).—Uses Mg instead of Zn for ores, slags, &c.
1663. CARNEGIE (Z. C. S., liii., 468).—Reduces by filtering through Zn dust. JONES (C. N., lx., 93).—Filters through pulverised Zn and illustrates its many advantages. See also SHIMER (Z. C. S., lxxviii., ii., 50).
1664. MACIVOR (C. N., xxix., 246).—Hæmatites readily dissolve as FeO on heating with H_2SO_4 and Zn, and so avoid HCl in the KMnO_4 titration.
1665. SCHMIDT (C. N., xlviii., 245).—Zn used to form FeO interferes with ferrocyanide indicator. SnCl_2 recommended.
1666. STORCH (Z. S. C. I., 1893, 866).—Reduce to FeO with Cu and titrate with KMnO_4 . Ignited Fe_2O_3 is soluble in 40 per cent H_2SO_4 .
1667. HART (C. N., xxxiv., 65).—Reduce ore to metal in H, dissolve in H_2SO_4 , and titrate with KMnO_4 . Or, dissolve in HCl , add excess SnCl_2 , and go back with I. MOISSAN (C. N., xl., 89).—After heating in H, Fe may contain FeO and Fe_3O_4 .
1668. REYNOLDS (C. N., x., 228).— H_2S is a better reagent for forming FeO than either Zn or SO_2 .
1669. ESILMANN (C. N., xxviii., 208).—Reduces Fe_2O_3 with Am_2S .
1670. LINOSSIER (C. N., li., 179).—Reduce with H_2S , destroy last traces by adding HgCl_2 , and titrate with KMnO_4 .
1671. WELLS and MITCHELL (C. N., lxxiii., 123).—Reduce with H_2S ; precipitated S no effect on KMnO_4 titration. Cu removed by filtration.
1672. AUSTEN and HURFF (C. N., xlvii., 287).—Résumé of Fe_2O_3 to FeO reductions; recommends Na_2SO_3 . Boil until steam no longer decolorises KMnO_4 . REINSCH (C. N., v., 126).—Cu wire by a brown coloration on its surface will detect one-millionth part SO_2 . BROWN (Z. C. S., liv., 267).—Tests for SO_2 by paper soaked in ferric chloride and ferrocyanide.
1673. ATKINSON (C. N., xlix., 117).—Bisulphite added to neutral solution best means of forming FeO. Errors due to Zn and SnCl_2 . Speed of ferrocyanide indicator and rate of decomposition.
1674. CLARKE (C. N., xvii., 234).—Fuse ore, slag, or cinder with bisulphate and cryolite, dissolve in HCl , reduce, and titrate with $\text{K}_2\text{Cr}_2\text{O}_7$.
1675. REINHARDT (Z. I. S. I., 1885, 299; 1889, i., 400; and 1900, i., 375).—Add SnCl_2 to hot acid Fe_2Cl_6 , destroy excess with HgCl_2 , add MnSO_4 , and then H_3PO_4 , so that Fe_2Cl_6 colour may not mask KMnO_4 end-reaction. See also BYA (C. N., lvi., 279) and MITCHELL (Z. S. C. I., 1894, 1096).
1676. CADY and RUDIGER (Z. I. S. I., 1897, ii., 508).— SnCl_2 reduction; accurate KMnO_4 titration in the presence of H_2SO_4 .
1677. NAMIAS (Z. I. S. I., 1892, i., 492).—Add excess $\text{K}_2\text{Cr}_2\text{O}_7$ to FeO solution, and a few drops of I and starch, and titrate with SnCl_2 .
1678. MIXER and DUBOIS (Z. I. S. I., 1895, ii., 60r).—Dissolve ore in $\text{HCl} + \text{SnCl}_2$, destroy excess SnCl_2 with HgCl_2 , and titrate with KMnO_4 .
1679. MAHON (Z. I. S. I., 1894, i., 617).—Pt carried by fusion flux into solution is reduced by SnCl_2 and leads to error.
1680. MITTENZWAY (C. N., ix., 253).—Measure O absorbed by alkaline FeO solution by weighing the water which runs into closed operating bottle.
1681. ROSS (Z. C. S., lxxii., ii., 193).—Add $\text{K}_2\text{Cr}_2\text{O}_7$ to FeO solution, and determine the excess by Baumann's process (1040).
1682. PARKER (C. N., xxii., 313).—Cu interferes with ferrocyanide indicator. Reduction of Fe_2O_3 with Zn would remove all the Cu.
1683. HOGG (C. N., lix., 207).—Cu in Fe alloys is not dissolved by dilute acids (see 1534) and reduces Fe_2O_3 as it is formed in the titration. Dissolve in $\text{HCl} + \text{KClO}_3$, and reduce with SO_2 .
1684. RIDEAL and ROSENBLUM (Z. S. C. I., 1896, 158).—Nickel gives a brown colour with ferrocyanide, which may mask the end-reaction with dilute FeO solutions. JERVIS (C. N., lxxvii., 133).—Mn acts similarly.
1685. BLUM (Z. I. S. I., 1900, ii., 582).—The almost unfailing presence of V in tap cinder interferes with volumetric determinations; gives elaborate gravimetric method.
1686. ATKINSON (C. N., xlix., 117).—Means of standardising $\text{K}_2\text{Cr}_2\text{O}_7$. The C in steel used for the purpose leads to low results (see 119).
1687. WELLBORN (C. N., xx., 57).— FeSO_4 is preserved from oxidation by placing camphor (in paper)

- therewith. GAWALOWSKI (C. N., xlvii., 165) uses pyrogallous acid similarly.
1688. VOGEL (C. N., xxiii., 142).—An exposure to direct sunlight for thirty seconds may cause ferricyanide to give a blue colour with ferric salts.
1689. STOCK (C. N., xxxix., 47).—A simple apparatus for effecting reductions out of contact with air.
1690. JOHNSON (C. N., xiv., 287).—FeO solutions are oxidised the more readily if external air is excluded; suggests that FeSO₄ has ozonising action on enclosed air.
1691. PATTINSON (C. N., xxi., 268).—Hot FeSO₄ solutions exposed to the air to cool are not appreciably, if at all, oxidised.
1692. WILLBUR and WHITTLESEY (C. N., xxii., 2).—Mix powdered silicate with CaF₂+HCl, heat in coal-gas, and titrate FeO with KMnO₄. ALLEN (C. N., xxii., 57).—Estimates FeO by digesting ore or sand in a closed tube with HCl.
1693. EARLEY (C. N., xxx., 169) and DÖLTER (C. N., xxxix., 135).—Decomposes silicate with HF, and titrates with KMnO₄ or K₂Cr₂O₇.
1694. PRATT (J. C. S., lxi., 482).—Dissolves silicate in HF+H₂SO₄ in CO₂ in a Rose's crucible.
1695. CHESTER and CAIRNS (J. C. S., liv., 196).—Use AmF+H₂SO₄ in CO₂ atmosphere.
1696. PENFIELD and FOOTE (J. C. S., lxxvi., ii., 305).—Determine FeO in tourmaline by fusing with borax in an inert atmosphere and titrating H₂SO₄ solution with KMnO₄.
1697. HILLEBRAND (C. N., lxxxii., 211).—Comparison of sealed-tube and HF methods of estimating FeO; the former often too high. See also C. N., lxxviii., 106.
1698. NEUMANN (J. S. C. I., 1887, 680).—Metallic Fe in slag, &c., is estimated by treating with acid and collecting the H evolved in a modified Lunge nitrometer.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 6th, 1902.

Dr. ARMSTRONG, Vice-President, in the Chair.

(Concluded from p. 94).

16. "The Solubilities of the Calcium Salts of the Acids of the Acetic Acid Series." By J. S. LUMSDEN, D.Sc., Ph.D.

It is well known that many calcium salts diminish in solubility with increase of temperature, and in order to obtain further information on this subject the solubilities of the salts of the acids of the acetic acid series have been carefully determined.

Calcium formate is anhydrous when in contact with its saturated solution, and gives a simple ascending curve of solubility. The calcium salts of the other acids of the series contain water of crystallisation, and all diminish in solubility with rise of temperature until a minimum point is reached, after which the solubility increases.

Of the salts of the normal acids only calcium acetate changes from one crystalline state to another between 0° and 100°, whilst both calcium isobutyrate and calcium isovalerate have double curves. With the exception of calcium formate all the salts which have been examined, when in contact with their saturated solutions at 100°, consist of crystals which contain one molecule of water.

The salts of the normal acids increase in solubility from formate to acetate and propionate, then decrease quickly with the growth in the number of carbon atoms, the salts

of the iso-acids being more soluble than those of the corresponding normal acids.

17. "The Equilibrium between a Solid and its Saturated Solution at Various Temperatures." By J. S. LUMSDEN, D.Sc., Ph.D.

The solubilities of the calcium salts of the acids of the acetic acid series were found to be all represented by curves convex to the temperature axis, indicating at first decrease then increase of solubility.

A curve of this shape is in no way anomalous, for by considering the action of heat on each of the factors which condition the equilibrium in a saturated solution, it is seen to be typically a normal curve.

The factors which produce equilibrium in a saturated solution are:—The affinity between solid and solvent, the thermal energy of the solid, and the pressure of the dissolved particles. By resolving the solubility curve, which is an exact representation of the resultant of these forces at different temperatures, into component curves representing the forces, the influence of temperature on each can be studied.

When each force varies directly as the temperature, the solubility curve is a straight line; when the rate is different it is a curve convex to the temperature axis.

Some experimenters have given curves of solubility concave to the temperature axis, but examination of several curves of that kind has shown that they have been produced by the joining of points on two convex curves, so cutting out the transition point.

By estimating the heat of solution at two points on a convex curve where the solubility is the same, it was found that the sensible heat was much less at the higher point. It was also found that the heat of solution at any temperature diminishes with the concentration, and that the direction of the solubility curve indicates the heat of solution in a saturated solution only, being positive on a descending and negative on an ascending curve.

18. "On the Union of Hydrogen and Chlorine. Part IV. The Draper Effect." By J. W. MELLOR and W. R. ANDERSON.

The momentary expansion which occurs when a mixture of equal volumes of hydrogen and chlorine is exposed to a flash of light is called, after its discoverer, the Draper effect.

This phenomenon is only produced when luminous rays impinge upon a mixture of approximately equal volumes of hydrogen and chlorine, but not upon chlorine alone, either under reduced or under ordinary pressures, or at temperatures between 15° and 100°. It is not produced when chlorine is mixed with steam, air, nitrogen, carbon dioxide, carbon monoxide, or methane. When the effect reaches a certain magnitude the mixture explodes. Although a few sparks bring about no measurable combination of the mixed gases, the joint effects of a great number of sparks at intervals of half-an-hour or of one hour is measurable, thus showing that chemical combination takes place during the Draper effect. The amount of combination depends not only upon the number but also upon the intensity of the sparks. The Draper effect appears to be due to some disturbance in the gas which attends chemical combination.

19. "Note on the Constitution of certain Organic Nitrates." By C. R. MARSHALL and J. H. WIGNER.

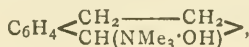
The authors criticise a theory recently advanced by Vignon and Gerin regarding the constitution of mannitol hexanitrate and allied substances. According to the French chemists, these higher nitrates reduce Fehling's solution strongly, whereas the lower nitrated compounds such as glycerol trinitrate have no reducing action whatever. In order to explain this they state that the terminal —CH₂OH group of the higher polyhydric alcohols is converted, during nitration, into a hydrated aldehyde group, —CH(OH)₂, which under the influence of the nitrous acid formed during the reaction, is further changed to a

—CH(OH)ONO group. This, by the action of the alkali of the Fehling's solution, is converted to an aldehyde group which acts as the reducing agent.

Against this view it is urged that the amount of nitrite formed during hydrolysis would vary considerably in the different members of the series, which is shown not to be the case. It is further proved that these compounds possess only a slight reducing action, which can be explained on other grounds. The authors see no reason for departing from the view that these substances are nitric acid esters of the various alcohols.

20. "Resolution of Trimethylhydrindonium Hydroxide into its Optically Active Components." By F. S. KIPPING.

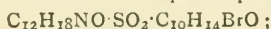
In continuing his work on hydrindamine (*Trans.*, 1900, lxxvii., 86f; 1901, lxxix., 370, 430, and 442) the author has studied some of the salts of trimethylhydrindonium hydroxide,—



in order to compare their behaviour with that of the salts of the parent base.

dl-Trimethylhydrindonium iodide (*Trans.*, 1900, lxxvii., 46g) interacts with silver d-bromocamphorsulphonate, giving dl-trimethylhydrindonium d-bromocamphorsulphonate, which can be separated into different fractions by crystallisation from a mixture of chloroform and ethyl acetate.

The most sparingly soluble fractions yield d-trimethylhydrindonium d-bromocamphorsulphonate,—



it crystallises in slender needles, melts at 199—200°, and in dilute aqueous solution $[\alpha]_D = +70^\circ$.

d-Trimethylhydrindonium iodide, $\text{C}_{12}\text{H}_{18}\text{NI}$, prepared from the preceding salt, crystallises from water in lustrous needles, decomposes at about 190°, and is very different from the racemic iodide in most respects; its specific rotation in dilute aqueous solution is $[\alpha]_D = +21.9^\circ$.

These results show that hydrindamine and trimethylhydrindonium hydroxide behave very differently towards one and the same acid.

21. "Resolution of Methylbenzylacetic Acid into its Optical Isomerides." By S. F. KIPPING.

Methylbenzylacetic acid, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ (α -methylhydrocinnamic acid), contains an asymmetric carbon group, is easily obtained in large quantities, and has recently been used for the preparation of methylhydrindone (*Proc.*, 1901, xvii., 181); in order to obtain an optically active acid chloride for various purposes indicated in the following note, the resolution of the acid was attempted.

Fractional crystallisation of the quinine salt gave the desired result; the salt of the d-acid is the more sparingly soluble in most solvents, and, after repeated crystallisation from dilute alcohol and ethyl acetate, is obtained apparently free from its isomeride.

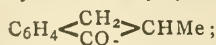
Quinine-d-methylbenzylacetate crystallises in prisms, melts at 118—119°, and is very readily soluble in warm alcohol, but only sparingly so in boiling water; it has a specific rotation $[\alpha]_D = -113^\circ$ in ethyl alcoholic, and $[\alpha]_D = -76^\circ$ in ethyl acetate, solution.

d-Methylbenzylacetic acid is an oil at ordinary temperatures; the highest specific rotation which has been observed with different samples of the acid (without solvent) is $[\alpha]_D = +20.3$. The sodium salt, purified by fractionally precipitating its alcoholic solution with ether, crystallises in colourless plates, and has a specific rotation $[\alpha]_D = +26^\circ$ in dilute aqueous solution.

The chloride, prepared by treating the d-acid with phosphorus pentachloride and distilling under reduced pressure, is optically active, but probably contains considerable quantities of the l-isomeride owing to partial racemisation having occurred.

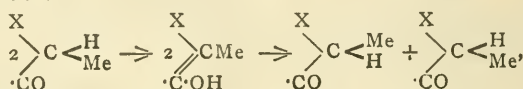
22. "d-Methylhydrindone. The Formation of Oximes, Hydrazones, and Semicarbazones." By F. S. KIPPING.

When the optically active methylbenzylacetyl chloride described in the preceding note is treated with aluminium chloride under suitable conditions (*Proc.*, 1901, xvii., 181) it yields an optically active methylhydrindone,—



the specific rotation of the crude product, which is probably a mixture of the d- and l-isomerides, is about $[\alpha]_D = +25^\circ$ in methyl alcohol.

The optical properties of the ketone seem to undergo no change at the ordinary temperature, so that it consists entirely of the keto-form; in accordance with this conclusion, it does not give a colouration with ferric chloride. When heated at its boiling-point under the ordinary pressure for some time the ketone racemises, doubtless owing to keto-enolic isomeric change. It also racemises when treated with small quantities of sodium methoxide, sodium hydroxide, or sodium carbonate in alcoholic solution, and the gradual change in rotation can be followed with the polarimeter. There can be little doubt but that this racemisation is brought about by a keto-enolic transformation.



and these observations afford direct experimental evidence in favour of the accepted views regarding such changes.

Methylhydrindone and hydroxylamine do not seem to interact in absence of alkali, but in presence of potassium hydroxide oxime formation occurs rapidly; the oxime obtained from the d-ketone is optically inactive. The d-ketone interacts with phenylhydrazine in acetic acid solution, giving a hydrazone; in this reaction also an optically inactive product is obtained. These facts seem to show that oxime and hydrazone formation are preceded by the conversion of the keto- into the enolic form.

When the active ketone is treated with semicarbazide hydrochloride and sodium acetate in aqueous alcoholic solution it yields an optically inactive and an active semicarbazone; the former is probably produced owing to the presence of the l-ketone in the original substance, and the formation of an active product seems to show that in semicarbazone formation there is no previous transformation of the keto- into the enolic modification. These and other reactions of ketones are being further investigated.

23. "Optically Active Methylbenzylacetic Acid." By A. LAPWORTH and W. H. LENTON.

In order to obtain further evidence on the question as to whether α -substitution in acids and ketones is the result of direct replacement of the hydrogen atom or is preceded by the formation of an ethylenic compound with the group $\cdot\text{C}::\text{C}\cdot\text{O}\cdot$, attempts were made to prepare an optically active acid which would undergo racemisation if the latter view were the correct one. For this purpose, methylbenzylacetic acid was thought to be the most convenient substance, as it is easily synthesised, and in its usual form is a solid at the ordinary temperature; the quinine salt of the acid was therefore fractionally crystallised from ethyl acetate until the melting-point and specific rotation of the least soluble portions remained constant.

Quinine d-methylbenzylacetate crystallised from ethyl acetate in well-formed needles which melted at 117°.

d-Methylbenzylacetic acid, $\text{CH}_2\text{Ph} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, is a colourless oil; its specific rotation in 1 per cent ethyl acetate solution was $[\alpha]_D = +14.9^\circ$. The ethyl ester, under similar conditions, has $[\alpha]_D = +13.2^\circ$.

The active acid does not racemise appreciably at temperatures below 130°, but when its chloride is brominated at 80—90°, the product is optically inactive.

As the authors learn from Dr. Kipping that he has been

engaged on the study of active derivatives of benzyl-methylacetic acid, they propose to leave its further investigation in his hands.

NOTICES OF BOOKS.

Practical Radiography; a Handbook for Physicians, Surgeons, and other Users of X-Rays. By A. W. ISENTHAL, F.R.P.S., and H. SNOWDEN WARD, F.R.P.S., Members of the Council of the Röntgen Society. Third Edition. London: Dawbarn and Ward, Ltd. 1901.

THE increasing application of Röntgen rays to medicine and surgery, and the many recent developments in the apparatus for their production, have rendered a third edition of this handbook necessary. To those engaged in radiography, or to any desiring sound information upon the subject, we can unhesitatingly recommend this third edition on account of its practical character, the authors having been actively connected with the application of Röntgen rays to surgery and other purposes from the time of their discovery. Between Chapters II. and XV. will be found a mass of valuable information. Induction coils, influence machines, interruptors, and other accessories to the production of the rays, are fully discussed, and descriptions are given of several little known pieces of apparatus, such as the Tesla oscillator, M.M. Rochefort and Wydt's coil, and the closed magnetic circuit coil recently exhibited in London. The valuable mercury jet interruptor, introduced by Dr. Max Levy, is exhaustively described and illustrated, as is also Wehnelt's electrolytic interruptor. The history and development of the Crookes tube is given in detail with a description of the method of manufacture. The most valuable part of the book is undoubtedly that devoted to the *technique* of radiography, and here will be found full details of the methods of charging accumulators, exciting coils, screen work, photography localisation, and stereoscopic radioscopy and radiography.

We are glad to see that the application of X-rays to therapeutical purposes is only briefly touched upon; this field, although it promises great results, is in a very early state of development.

It is a pity to have to find fault with an otherwise trustworthy work, but some rather wild statements have found their way into the introductory and theoretical chapters. These need not have been introduced at all, but having been introduced they should have been carefully revised. On page 8 we are told that the vibrations of ether produce heat, light, magnetism, and *gravitation*, and that all these manifestations of ether vibrations can "be ranged in a sequence which we call the spectrum," and further down on the same page, "a solution of bisulphide of carbon, which to luminous radiations is completely opaque, offers no obstruction to dark heat waves." Here the solution of iodine in bisulphide of carbon is meant. Many other slips occur in this part, and in Chapter XV. appears a discussion of Professor J. J. Thompson's "corpuscle" theory that indicates confusion in the minds of the authors. However, apart from these minor faults, the book is undoubtedly one of the best that has yet appeared on the technology of radiography, and will be found of great value both to the operator and the student. There is a good index and it is well illustrated.

The Methods of Glass Blowing and of Working Silica in the Oxy-gas Flame. For the Use of Chemical and Physical Students. By W. A. SHENSTONE, F.R.S. Fourth Edition, Re-issue, with new Chapter. London: Longmans, Green, and Co. 1902.

THIS handbook is simply a reprint of that issued in 1886, with the addition of a short chapter on the method of working silica in the oxy-gas blowpipe for the formation

of chemical and physical apparatus. Mr. Shenstone's success in working with quartz is so well known that any one desirous of fabricating quartz apparatus will gladly avail themselves of the practical experience detailed in this part of the book. The working of silica is not at all difficult, and with a little practice it will be found possible to produce rods, tubes, bulbs, and even small vacuum tubes from this material.

The Experimental Study of Gases; an Account of the Experimental Methods involved in the Determination of the Properties of Gases and of the more Important Researches connected with the Subject. By MORRIS W. TRAVERS, D.Sc., Assistant Professor of Chemistry and Fellow of University College, London. London and New York: Macmillan and Co. 1901.

THE above work being the outcome of researches carried out at University College during the past few years needs little further recommendation. It will be found full of descriptions of the apparatus and methods devised by the professors and assistants at that institution; many details of gas manipulation are described for the first time, well illustrated with original drawings. The collecting together with the latest corrections and modification of the mass of data that has been published at various times connected with the recently discovered gases of the atmosphere, will prove of considerable value to future investigators. We are sorry to note that for some unexplained reason all the promised plates of "*prism spectra of certain gases*," said to have been specially photographed for the book, are omitted, as are also Figs. 130 and 131; this is unfortunate as the photographed spectra in question are possibly the most valuable item in the description of the new gases.

There is an introductory preface by Professor Ramsay, a table of contents, and a good index.

The Cyanide Process of Gold Extraction. A Text-book for the Use of Mining Students, Metallurgists, and Cyanide Operators. By JAMES PARK, Professor of Mining and Director Otago University School of Mines, F.G.S., M.I.M.M., &c. Second English Edition, Revised and Enlarged. With Frontispiece, Plates, and Illustrations. London: Charles Griffin and Co., Ltd. 1901. Pp. 166.

SO short a time having elapsed since the publication of the first English edition of this book there is obviously little we can add to the remarks we made in these columns when reviewing the previous edition (CHEMICAL NEWS, vol. lxxxii., p. 157, September 28, 1900).

There are, however, a few points which merit attention. During the past two years the most noteworthy advances in the cyanide process have been in the treatment of slimes and sulphotelluride ores. The success of the new processes having been well-assured by actual experiment, the author has taken the opportunity afforded by this new edition to give a detailed description of the most up-to-date plants in South Africa, the United States, New Zealand, and Australia.

In Western Australia the oxidised ores are being replaced in depth by sulphide ores in which the gold is associated with tellurium, and the problem of treating these sulphotelluride ores is one of vital importance to many mines, especially to those of comparatively low grade.

There are two systems of treatment in use; the "raw ore" and the "roasted ore." In the former, introduced by Dr. Diehl, the ore is dry-crushed, then mixed with water, and, after amalgamation, ground to slimes in a large mill; the pulp is led to settling vats and the surplus water drawn off; the thickened pulp is then agitated with a solution of cyanide and bromide of potassium for twenty-four hours, then dried in a filter-press in which the dissolved gold is washed out. It is claimed that 93 per cent

of the gold can be recovered. The main features of the "roasted ore" treatment are drying, dry-crushing, roasting in a Ropp, Edwards, or other furnace, amalgamation in pans, cyaniding sands, if any, in vats, and the slimes in agitators; then filter-press separation, and washing of slimes. This latter process does not appear to us to be so simple or so economical as that of Dr. Diehl, as it necessitates much more "handling" of the ore. Both these methods are fully described, and plans of the plant used are given.

At the close of our remarks when dealing with the first edition of this book, while strongly recommending it, we ventured the opinion that "there will no doubt be a very large extension of mining operations when the pacification of the Transvaal has been completed, and the demand for really skilled managers and metallurgists will be greater than it has ever been before." We still adhere to that opinion, and though we were, like many others, a "little too previous," the very fact that more mills are getting to work every week round Johannesburg, and that the gold output for January last was over £250,000 in value, shows that the "good time coming" cannot now be very far off.

Mixed Metals, or Metallic Alloys. By ARTHUR H. HIGGINS, Head of Metallurgical Department, Birmingham Municipal Technical School. Second Edition. Completely Revised and Enlarged. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1901. Pp. 445.

SINCE the first edition of this book was published in 1890 great advances have been made in the study of alloys, notably by Sir W. Roberts-Austen, Mr. Stead, MM. Charpy, Le Chatelier, Moissan, and other well-known chemists. And in this, the second edition, numerous references have been made to the published works of these and other eminent authorities. It is pointed out that the scientific study of alloys has not yet been sufficiently matured to permit of placing the subject on a logical scientific basis, and judging by the experience of different branches of applied chemistry, such as dissolution, fractional distillation, dissociation, &c., it will take many years to enable the new theories to be properly sifted, tested, and co-ordinated, as well as to connect such a scientific basis effectively with practical industry.

The principal chemical elements are first dealt with, and their classification into suitable groups; then the refractory materials used in making crucibles and in furnace construction, as well as the properties and uses of various fluxes, are described.

The alloys themselves are arranged in the following order:—(1) Copper alloys; (2) nickel alloys; (3) tin alloys; (4) lead alloys; (5) mercury alloys, or amalgams; (6) alloys of precious metals, including gold, silver, and platinum; (7) iron alloys; and (8) miscellaneous alloys. Under one or other of these headings will be found, besides the metals already named, alloys containing bismuth, antimony, arsenic, aluminium, nickel, cobalt, manganese, tungsten, titanium, sodium, potassium, and magnesium.

The book is intended essentially as a guide to manufacturers, workers, and students, and by the help of its copious index the reader will be able to find any particular alloy or mixture he desires with a minimum of trouble.

An Introduction to Chemistry and Physics. Two Vols. By W. H. PERKIN, JUN., Ph.D., F.R.S., and BEVAN LEAN, D.Sc., B.A. (Lond.) London: Macmillan and Co. New York: The Macmillan Company. 1901.

THIS second edition of a useful little book contains a good deal of new matter, and is divided into two volumes, the first providing a first year's course of physics, and the second dealing chiefly with chemistry. The book represents an attempt to follow the lines of historical development in initiating the young learners in the rudiments of

these sciences, and thus it is hoped to foster the spirit of research always latent in the young, and to develop the power of reasoning from observation—the true aim of all scientific education. No one will be found to deny that the old way of teaching chemistry was unscientific, and often led to a distaste for a subject which entailed loading the memory with so many apparently disconnected facts; the new method minimises the efforts of memory, constantly calling the reasoning powers into play, and this book is a very good exponent of this system. The first volume is perhaps the better, being thoroughly practical and reliable throughout, while some parts are really excellent; for example, the chapter on "Graphic Representation" is most lucid and useful. The second volume will perhaps prove most valuable in the hands of a good teacher, whose aim should always be to make the learner find out as much as possible for himself. Many experimental details, such as the best way of collecting gases free from air, may be elicited from the learners themselves by dint of judicious questioning. It is, however, exceedingly difficult to dispense with the use of a text-book altogether in class-teaching, and this book can be thoroughly recommended as an excellent first course in physics and chemistry. The chapter on fuel and food-stuffs is practical and useful, and the account of Black's researches on chalk is specially good. Frequent problems and exercises intersperse the text, all probably well within the limits of time and capability of the learners, and a few examination papers enhance the book's usefulness.

Beiträge zur Chemischen Physiologie und Pathologie. Edited by FRANZ HOFMEISTER. Band I., 10-12 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1902.

THE January number of the *Journal of Chemical Physiology and Pathology* brings to an end the first volume, and contains the index. One paper of this number gives the results of the investigation and ultimate analysis of the albumens and cell membranes of bacteria and fungi, isolated by Krakow's new method recently communicated to the St. Petersburg Medical Society, and shorter papers deal with the subjects of the formation of sugars from protein substances, and the decomposition of guanidine by the animal body. Other articles of mainly physiological interest point to the great activity of investigators of this branch of science, in which so much work is still to be done.

CORRESPONDENCE.

THE SOCIETY OF PUBLIC ANALYSTS.

To the Editor of the Chemical News.

SIR,—In view of the press reports of the proceedings at a recent Dinner of the Society which is still incorrectly called the "Society of Public Analysts," we venture to ask you to give publicity to the following statement.

The title "Public Analyst" is legally applicable only to certain scientific officers, appointed by specified public authorities under the provisions of the Sale of Food and Drugs Acts, whose qualifications have been approved and whose appointments have been sanctioned by the Local Government Board.

At the present time only about 28 per cent of the members of the Society referred to are Public Analysts, owing to the fact that, as stated by its President, "the Society has widened its borders and now includes other analytical chemists" and persons concerned "with all branches of the chemical industry"—an expression of obviously wide application. The President is also reported to have said that "the great object of the Society was to ensure that its members were possessed of proper qualifications"—a

statement which, if left uncorrected, may cause serious misapprehension.

The Society in question is not, in any sense, a qualifying body, and its rules contain no specific requirements as to the scientific qualifications of candidates for admission to it, beyond the mere fact that each candidate must be recommended by three of the members, who testify "from personal knowledge" to his "scientific fitness." Indeed, one of the previous Presidents of the Society, when under examination before the late Food Products Committee of the House of Commons, found himself compelled to admit that membership of the Society did not imply the possession of any special qualifications.

The only qualifying body connected with the profession of Analytical and Consulting Chemistry is the Institute of Chemistry of Great Britain and Ireland, which was incorporated by Royal Charter in 1885, and which, under that charter, grants diplomas of Associateship and Fellowship to candidates who, having gone through prescribed courses of study and training, have passed the examinations conducted by the Institute.

From the facts stated above it will be seen that the Society referred to does not and cannot properly represent the Public Analysts of the country, that it cannot justifiably be described as a "Society of Public Analysts," and that it is in no sense a qualifying body.—We are, &c.,
(Signed)

J. CARTER BELL, Public Analyst for the County of Cheshire, and the Boroughs of Salford, Birkenhead, &c.

CHARLES E. CASSAL, Public Analyst for the City of Westminster, the Royal Borough of Kensington, the Metropolitan Borough of Battersea, and the County of Lincoln (Kesteven and Holland Divisions).

J. KEAR COLWELL, Public Analyst for the Metropolitan Boroughs of Finsbury and Holborn, and the Borough of Bedford.

C. HOWARD CRIBB, Public Analyst for the City of Westminster, and the Metropolitan Borough of Fulham.

W. F. KEATING STOCK, Public Analyst for the County of Durham, and the Borough of West Hartlepool.

February 22, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 5, February 3, 1902.

New Synthesis of Formic Acid.—Henri Moissan.—The author has already shown that potassium and sodium hydrides, when slightly heated, react on carbonic acid gas, liberating carbon. The reaction produced with potassium hydride, when this latter is in the form of small crystals, causes sufficient heat to be evolved to bring the hydride to the point of incandescence. When sodium hydride is used, and a jet of carbonic acid is allowed to play on this hydride kept at the ordinary temperature, it is seen to suddenly burst into flame. This spontaneous combustion of an alkaline hydride in presence of carbonic acid leads the author to prepare formates by a new synthetic method.

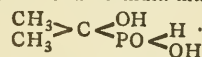
Comparison between the Properties of Seleniuretted Hydrogen and those of Sulphuretted Hydrogen.—MM. de Forcrand and Fonzes-Diacon.—The authors measure various constants of the two gases, hydrogen selenide and hydrogen sulphide, using very pure specimens

prepared by themselves. The constants are given in the following table:—

	H ₂ S.	H ₂ Se.
Temperature of ebullition (T) at 760 m.m. pressure (absolute)	211.4°	231°
Critical temperature (T _c)	373.2°	410°
T/T _c	0.566	0.564
P _c (critical pressure)	92 at.	91 at.
T' (fusion temperature)	187°	209°
D (density of the liquid at boiling-point)	0.86	2.12
PM/D (liquid molecular volume)	39.53	38.11
L (heat of volatilisation)	4230 cal.	4740 cal.
L/T (Trouton's relation)	20.01	20.52
C (heat of formation of hydrate)	16,340 cal.	16,820 cal.
t (temperature for which the hydrate has a tension of 760 m.m.)	273.35	281
S (solubility at +4.00°)	4.04 vols.	3.77 vols.
" " +9.65°)	3.60 "	3.43 "
" " +13.2°)	3.35 "	3.31 "
" " +22.5°)	2.75 "	2.70 "

Action of Lithium-ammonium on Antimony and Properties of Lithium Antimonide.—P. Lebeau.—Lithium-ammonium reacts on antimony, giving a compound having the formula SbLi₃, the same product as that obtained by electrolysis. This body dissolves in liquid ammonia and unites with it to form the compound SbLi₃.NH₃. Lithium antimonide is considerably less fusible than its constituent elements. This peculiarity is much the same as was observed for aluminium antimonide by Henri Gautier. Finally, this compound possesses very energetic reducing properties.

Oxyisopropylhypophosphorous Acid.—C. Marie.—A study of oxyisopropylhypophosphorous acid and its derivatives shows that it is a monobasic acid, to which, by analogy with M. Ville's oxybenzylhypophosphorous acid, the following constitutional formula may be attributed:—



Hydrolysis of Pyromucic Urethane.—R. Marquis.—M. Freundler prepared pyromucic hydrazide and azide, and established the formation of red condensation products by the action of dilute hydrochloric acid on the product of the action of the alcohol on the azide. The author applies this method of hydrolysis to the methylic and ethylic urethanes.

Action of Nitric Acid on Trichlorated and Tribromated Veratrols.—H. Cousin.—The action of nitric acid on the trichlorated and tribromated veratrols gives rise to mononitrated derivatives of tri-substituted veratrols. In this case the reaction is totally different from that obtained with the tetrachlorated and tetrabromated veratrols, because in that case tetra-substituted orthoquinones are formed by saponification of the ether functions and oxidation of the corresponding phenols. The action of nitric acid on the tri-substituted veratrols can be compared with the reaction of nitric acid on dibromated veratrol, which gives, as the author previously noticed, a mononitrated dibromated veratrol. Such a reaction is totally different from that obtained with the trisubstituted galacols, which, when treated with nitric acid, give diphenyl derivatives—compounds which contain no nitrogen and belong to the class of the quinones.

Some Derivatives of Glucamine.—E. Roux.—In a previous paper the author described a derivative of glucose, called glucamine, which possesses the formula NH₂CH₂(CHOH)₄CH₂OH. He now prepares a number of new derivatives of this base:—Cuproglucamine (C₆H₁₁O₅NCu₂), the picrate, chloroplatinate, chlorohydrate of pentacetylglucamine, hexacetylglucamine, benzalglucamine, glucamine-urea, glucamine-phenylurea, and pentacarbamic glucamine-phenylurea.

Action of Aluminium Chloride on certain Anhydrides in Chloroform Solution.—Marcel Desfontaines

—The author finds that anhydrous aluminium chloride acts in all cases like sulphuric acid on the anhydrides representing a tertiary carboxyl, such as the *aa*-dimethylglutaric and *aa*-dimethylsuccinic anhydrides.

MISCELLANEOUS.

Society of Chemical Industry.—As the Annual Meeting of the Institute of Chemistry is to be held on Monday, March 3rd, the next Meeting of the Section has been postponed from that date to Monday, March 10th, The Meeting will then be held at the Chemical Society's Rooms, Burlington House, Piccadilly.

Acetylene Lighting at a London Board School.—Mr. John C. Christie, of Aldgate, Gas Contractor to the London School Board, is at present fitting up the new Board School at Fulham Palace Road with acetylene. A portion of the school has been handed over for use, and the installation has proved most successful. The generators and purifiers used are of the Thorn and Hoddle Acetylene Co., Ltd., of Westminster, manufacture.

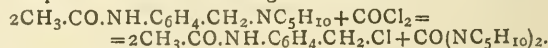
Small-pox Insurance.—Through the enterprise of Charles Letts and Co. (3, Royal Exchange, E.C.), of Diary fame, a small-pox insurance in combination with an excellent Note Book has been placed on the market for the nominal sum of one shilling. The insurance is for £100 in the event of the disease terminating fatally, with weekly allowance during illness (limited to five weeks). As the shilling also includes an excellent Note Book, with back loop, pencil, and elastic band, or, if preferred, a Card Case with stamp pockets, &c., the value is apparent, and particularly so to medical men. Unlike Lloyds and other insurance companies, Letts's coupons do not place doctors on an entirely different footing to the general public, demanding from the profession a largely increased premium for the risk covered. Our readers, therefore, cannot do better than to send to their stationers or to Messrs. Letts for a copy.

The Preparation of Tantalum by means of the Electric Furnace, and its Properties when thus Prepared.—Henri Moissan.—Powdered niobite mixed with sugar-charcoal, when subjected to the temperature of the electric furnace, yields a substance rich in niobium and tantalum. The metallic mass, treated first with a mixture of nitric and hydrofluoric acid, then with potassium fluoride, gives a mixture of fluotantalate and fluoxyniobate. The author separates these by Marignac's method, and decomposes the fluotantalate by sulphuric acid in a platinum capsule. After repeated purification, the tantalic acid is mixed with sugar charcoal and placed in the electric furnace: $Ta_2O_5 + 5C = 2Ta + 5CO$. The tantalum is obtained in the form of a brilliant metallic mass. The various properties of the metal which are examined show it to possess very strong reducing properties. Its reactions resemble those of niobium very closely; the increased reducing action being the only difference noticed between the two metals.—*Comptes Rendus*, cxxxiv., No. 4.

Investigation of Aluminium-Iron and Aluminium-Manganese Alloys.—Léon Guillet.—The author undertakes a systematic study of the alloys of aluminium with iron and manganese by reducing the oxide by aluminium in presence of excess of the latter. His experiments show—(1) That the limit of inflammability takes place when a mixture corresponding to the formation of the compound $FeAl$ is used. However, in a Perrot's furnace the limit of inflammability may be extended until the theoretical formation of the compound $FeAl_4$ is reached. (2) All these reactions take place without loss, and they are slow. (3) The metallic globules are always very small, except in those experiments giving theoretically $FeAl$ and $FeAl_4$. (4) The products prepared contain 2 to 15 per cent of free aluminium. (5) All the melts containing the metals in proportions between those giving theoretically $FeAl$ and $Fe_{10}Al$ fall rapidly into powder. (6) All the melts ob-

tained from the experiments comprised between the proportions corresponding to $FeAl_2$ and $FeAl_4$ give magnificent prismatic crystals whose length attains 6 or 8 cm. The following compounds were isolated and analysed:— Fe_2Al_3 , $FeAl_3$, Mn_2Al_3 , $MnAl_3$, $MnAl_4$.—*Comptes Rendus*, cxxxiv., No. 4.

A New Reaction of Phosgene.—B. Kühn.—The author has found, in collaboration with Spindler and P. von Gartzon, that phosgene is capable of breaking the bond between one atom of carbon and the tertiary aminic nitrogen; the valences set free are saturated by $>CO$ and $Cl-Cl$. This phenomenon appears to bear a strong resemblance to hydrolysis, and probably depends on the dissociation of phosgene into ions. The authors have examined the reaction with the acetylated derivatives of the ortho-, meta-, and para-amidobenzylpiperidines which are split up by the action of phosgene at the ordinary temperature in the following manner:—



This decomposition allows of the preparation of the chlorides of the acetylated ortho-, meta-, and para-amidobenzyls which are very susceptible to the reaction. The acetylated derivatives of the amidophenylpiperidines do not react in this manner, neither does benzoylpiperidine, which is, however, so easy to hydrolyse; for this reaction to take place it seems necessary for the piperidinic nitrogen to be united to the methanic carbon deprived of oxygen.—*Berichte*, vol. xxxiii., p. 2900.

The Bromination of the Mixed Hydrocarbides.—A. Erdinger and P. Goldberg.—The authors have established the following method for the bromination of the mixed hydrocarbides:—100 c.c. of HNO_3 ($D=1.4$) are added to a solution of 25 grms. of the hydrocarbide to be bromised, in 100 c.c. of benzene; they then introduce, very gradually during two or three hours, an excess of bromide of sulphur; when the whole of the bromide has been added they decant the benzene solution, and shake well with caustic potash; the benzene is then distilled off, and the bromised derivative separated by distilling the residue with steam and fractionating over potash. This method gives, with a return of 85 to 95 per cent of theory, monosubstituted products with the exception of durol, with which they have always obtained, up to the present, a dibromised derivative. In this manner the authors have prepared bromobenzene (in this case an excess of benzene must be used), bromotoluene, the bromoxylenes, bromomesitylene, bromopentamethylbenzene, and bromonaphthalene; they also describe the dibromodurol which forms the exception.—*Berichte*, vol. xxxiii., p. 2883.

MEETINGS FOR THE WEEK.

- MONDAY, March 3rd.—Society of Arts, 8. (Cantor Lectures). "Photography applied to Illustration and Printing," by J. D. Geddes, F.R.P.S.
—Royal Institution, 5. General Monthly Meeting.
- TUESDAY, 4th.—Royal Institution, 3. "The Temperature of the Atmosphere—its Changes and their Causes," by W. N. Shaw, M.A., F.R.S.
—Society of Arts, 8. "Structural Colour Decoration of the Interior of Public Buildings," by Gerald C. Horsley.
- WEDNESDAY, 5th.—Society of Arts, 8. "Sound Signals," by E. Price Edwards (Trinity House).
- THURSDAY, 6th.—Royal Institution, 3. "Scotland's Contribution to the Empire," by Sir Henry Craik, K.C.B.
—Chemical, 8. "The Slow Oxidation of Methane at Low Temperatures," by W. A. Bone and R. V. Wheeler. "Isomeric Additive Compounds of Dibenzyl Ketone and Deoxybenzoin with Benzal-p-toluidine, *m*-Nitrobenzalaniline, and Benzal-*m*-nitraniline" (Part III.), by F. R. Francis. "Mesoxalic Semi-aldehyde," by H. J. H. Fenton and J. H. Ryffel. "*m*-Nitrobenzoylcamphor," by M. O. Forster and F. M. G. Micklethwait. "Picrimidithiocarbonic Esters," by J. C. Crocker.
- FRIDAY, 7th.—Royal Institution, 9. "Radio-active Bodies" (in French), by Prof. H. Becquerel, D.C.L., Ph.D., Membre de l'Institut, Paris.
- TURSDAY, 8th.—Royal Institution, 3. "Some Electrical Developments," by Lord Rayleigh, F.R.S., &c.

THE CHEMICAL NEWS.

Vol. LXXXV., No. 2206.

RADIO-ACTIVITY AND THE ELECTRON THEORY.*

By Sir WILLIAM CROOKES, F.R.S.

ELECTRONS emanating from radio-active bodies behave like material particles, and are impeded by the molecules of the surrounding medium, in contrast with ether waves, which are not thus affected except by absorption. It is not difficult to put these indications to test. A pair of shallow cells, A B (Fig. 1), 1.5 m.m. deep and 25 m.m. square, were made by cementing slips of glass to a thick glass plate. The cells were filled to the same depth with a radio-active substance chiefly containing actinium.† Over cell A was placed a piece of thick lead pipe, 28 m.m. high and 25 m.m. internal diameter, to ensure that any emanations from the active substance in A would be confined to the inside of the hollow cylinder. The radio-

a strong impression over cell A and none over cell B. The figures were:—

Opacity log. = 0.89; Opacity = 7.71.

These experiments indicate that the electrons from the radio-active agent, chiefly actinium, partake of the properties of a fog or mist of material particles, capable of diffusing away in the free air like odoriferous particles, when not kept in by a thick metal screen.

A further experiment was now tried with the same apparatus, the agent a strongly active radium and barium bromide. This material being self-luminous, a sheet of black paper was placed immediately over it, so that nothing but emanations capable of passing through the opaque paper would be subject to experiment. After four hours' exposure in total darkness the film was developed. A good circular patch was obtained over cell A, and a faint diffused darkening showed over the rest of the film, darker at the spot immediately over cell B, fading away at the sides as the distance became greater. That this action was due to the material in the open cell B, and not to general fog over the plate, was seen by the clearness of the film where covered by the lead, and where shadows were thrown by the lead cylinder and pillar.

Circles of the same diameter were drawn round the dark impression over A, and round the darkest part of the impression over cell B. Measurements were taken of

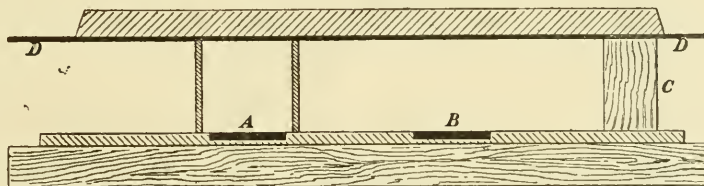


FIG. 1.—Elevation.

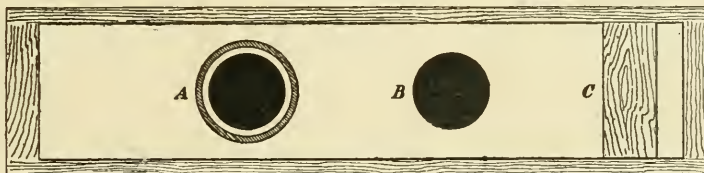


FIG. 1.—Plan.

active substance in B was freely exposed to the air, save for a pillar of lead at C, to support the sensitive film. A sensitive film was laid horizontally over the cylinder and support C. On the film was a plate of glass, and cylinder and film were pressed together by heavy weights. The whole was covered in a light-tight box and put in a dark cupboard.

At the end of forty-eight hours the film was removed and developed. There was a strong action shown over cell A (the one covered by the lead cylinder), but over B, the cell exposed to the air, there was no visible impression. Measured in Mr. Chapman Jones's "Opacity Meter" (*The Photographic Journal*, vol. xx., p. 86, Dec. 21, 1895), the results were:—

Image over cylinder—Opacity log.‡ = 0.79; Opacity§ = 6.17.

The experiment was repeated, using the same apparatus but a different preparation of actinium. In this case the exposure was for seventy-two hours. As before, there was

different parts of the spaces enclosed in these circles, and the mean of all these came out—

Circle over cell A—Opacity log. = 0.53; Opacity = 3.39.

Circle over cell B—Opacity log. = 0.32; Opacity = 2.09.

Ratio B/A = 0.62.

The experiment was repeated with the addition of a sheet of aluminium, 0.02 m.m. thick, under the black paper, the electrons now having to pass through both paper and metal before reaching the film. The exposure was for six hours, and the appearance on development was very similar to the last; a dark disc over the protected cell A, and a diffused action over the other part of the film, except in the shadow of the lead supports. Measurements as on the previous occasion gave the following results:—

Circle over cell A—Opacity log. = 0.78; Opacity = 6.03.

Circle over cell B—Opacity log. = 0.48; Opacity = 3.02.

Ratio B/A = 0.5.

A third experiment was tried with the same apparatus, using only the aluminium plate as a screen to cut off the luminous rays. The appearance on development was similar to the others, and the measurements of opacities were—

Circle over cell A—Opacity log. = 0.59; Opacity = 3.89.

Circle over cell B—Opacity log. = 0.29; Opacity = 1.95.

Ratio B/A = 0.5.

* A Paper read before the Royal Society, February 6, 1902.

† The body I called Uranium X in my Royal Society paper, May 10, 1900, has since proved to be M. Debierne's Actinium.

‡ The opacity logarithm represents the density of the image, absolute density being represented by 2.00.

§ The "opacity" is the whole number corresponding to the "opacity log." The "opacity" is directly proportional to the photographic energy acting on the sensitive surface.

Finally, I tried polonium subnitrate, which gives off emanations hardly capable of passing through any screen, and greatly obstructed by a few centimetres of air.

The apparatus was substantially the same as the one just described, with the modification that the lead cylinder was 12 m.m. high, and at the other end a rod of glass 12 m.m. high was used to support the film. The reduced height was chosen, experience showing that polonium emanations have great difficulty in penetrating many millimetres through air. The exposure was seven days, at the end of which time the film was developed. Over cell A a dark disc sharply defined the inside of the cylinder, while over cell B was a hazy diffused patch which to the eye looked much the fainter of the two. But measurements of patch A and of a disc over cell B of the same size as A, showed that the opacities in each case were practically identical, as shown by the following figures:—

Circle over cell A—Opacity log.=0.74; Opacity=5.49.

Circle over cell B—Opacity log.=0.76; Opacity=5.75.

Ratio B/A=1.05.

A repetition of the experiment, taking the mean of five concordant results, gave the same opacities as before.

Without proving that the emanations from polonium are less material than those from actinium and radium, this experiment shows that their behaviour is entirely

different as regards diffusibility through air. Whether this is due to the larger mass of the individual particles, or to the less distance they have to travel (12 m.m. as against 28 m.m. in the case of actinium and radium), or to some other cause, further experiments must decide.

M. and Mme. Curie have shown that radio-activity is communicable from radium and actinium compounds to bodies such as lead, copper, glass, ebonite, and paraffin. After exposure to emanations from the radium compound, these bodies have the property of communicating temporary conductivity to the air and other gases, and of thereby discharging an electrified body.

When such charged bodies are exposed to the air, in a single day they lose the greater part of their activity. These phenomena are observed with different radio-active salts of radium, also with salts containing actinium; but polonium compounds, even when very active, do not communicate the effect.

Dr. Rutherford shows that air which has remained for some time in the neighbourhood of thorium and then is carried in a current to a distance, retains its property of communicating radio-activity to other bodies. He explains these phenomena by supposing that thorium gives off a special kind of emanation capable of being conveyed by the air, and that this is the cause of the induced radio-activity.

To ascertain if the electrons or corpuscles from radium also possess the property of being carried along in a cur-

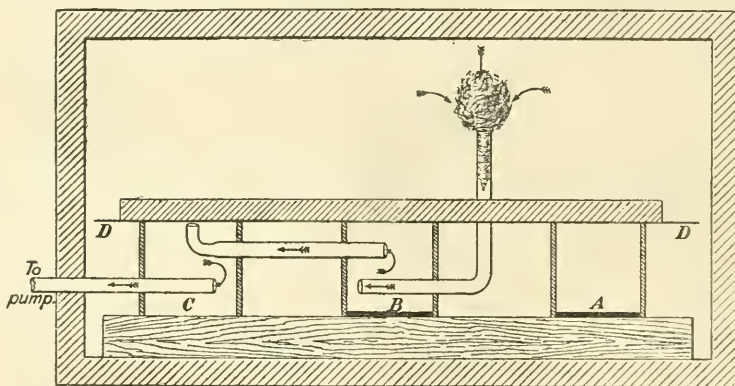


FIG. 2.—Elevation.

rent of air, I fitted up an apparatus shown in Fig. 2. A, B, and C are three brass tubes closed at the lower end and cemented with paraffin to a wooden block. The upper ends were accurately ground to a level surface, and then coated with a thin layer of paraffin wax. Holes were drilled in B and C, to admit glass tubes, cemented air-tight into the cylinders, as shown in the figure. The upper end of the tube in B was closed with a plug of cotton-wool, and the outer end in C was connected to a water-pump, so that when the cylinders were closed at the top a current of air was drawn through B and C. As the radium compound was self-luminous, discs of thin aluminium foil were placed over cylinders A and B to cut off the luminous rays. A sensitive film was laid on the three cylinders over the aluminium, and it was tightly pressed down by a heavy weight; the contact between the film and the tops of the cylinders being sufficient to make the whole air-tight. At the bottom of A and B a radium compound was placed, equal weights and equal surface in each. The whole was put into a light-tight box, and air drawn through. The cylinder A was used only as a standard. The air passing into B was expected to carry along with it some of the corpuscles emitted from the active material at the bottom; and the inlet tube in C was turned up at the end, so that the stream of corpuscles-laden air should impinge on the surface of the centre of the film on C, and

if it carried with it any radio-active properties the result should be seen on development, by the production of a dark patch. If, however, the air carried no corpuscles there would be no image on the sensitive film over C.

The experiment was continued for eleven hours, 120 litres of air having passed through in the time.

On development and measuring the resulting images the following figures were obtained:—

Circle over cell A—Opacity log.=0.342; Opacity=2.20.

Circle over cell B—Opacity log.=0.178; Opacity=1.51.

Circle over cell C—Opacity log.=0.025; Opacity=0.11.

Ratio B/A=0.68.

The apparatus was slightly altered. Cells B and C were put nearer together, and a short wide brass tube replaced the turned-up glass tube formerly connecting them. The experiment was continued for forty-eight hours, during which time about 500 litres of air passed through the apparatus.

This repetition, allowing longer time, gave measurements as follows:—

Circle over cell A—Opacity log.=0.964; Opacity=9.20.

Circle over cell B—Opacity log.=0.730; Opacity=5.37.

Ratio B/A=0.58.

In this experiment a slight but measurable darkening took place over cell C, shown by an opacity log. of 0.025 and an opacity of 0.11. This shows that some few cor-

puscles from radium also possess the property of being carried along in a cur-

puscles have been able to pass through the wide tube from B to C, and act on the photographic film.

It thus appears that a current of air passed over the surface of a radium compound carries with it a certain proportion of the corpuscles. This is proved by the diminished photographic action in the second cell, slightly confirmed by the evidence that some few of the corpuscles so carried away get to the sensitive film on cell C. Judging from our slender knowledge of the properties of free electrons, it is highly probable that they will not easily turn a corner, but cling to the sides of the tube through which they are being led. On the other hand, the constant collisions with the atoms of air may reduce their initial mobility almost to a vanishing point before they have travelled along the tube between B and C, and then they would be carried along with the air.

The experiment was repeated, using a preparation of actinium (Uranium X). It was kept going for seventy-two hours, during which time 750 litres of air were drawn through the apparatus. On development and measurement the following results were obtained:—

Circle over cell A—Opacity log.=0.99; Opacity=9.78.

Circle over cell B—Opacity log.=0.67; Opacity=4.68.

Circle over cell C—Opacity log.=0.25; Opacity=1.78.

Thoria prepared by the ignition of Dr. Knöfler's highly purified thorium nitrate (*Roy. Soc. Proc.*, vol. lxvi., p. 421, May, 1900) was now tested in a similar apparatus to the one last described, the only alteration being the removal of the covering aluminium plates, thoria not being self-luminous. The experiment was continued for one hundred and eight hours, 1125 litres of air being drawn through the cells during the time.

Measurements of the developed images gave the following results:—

Circle over cell A—Opacity log.=0.306; Opacity=2.02.

Circle over cell B—Opacity log.=0.260; Opacity=1.82.

Circle over cell C—Opacity log.=0.046; Opacity=0.10.

Here also the results agree with those tried with radium and actinium compounds, that corpuscles are carried by a current of air from cell B, through the connecting tube to cell C. They also confirm those of Dr. Rutherford—who finds that thorium emanations travel in a current of air while retaining their activity—and of P. Curie and A. Debierne, who show that induced radio-activity can be transmitted through capillary tubes of an internal diameter of 0.1 m.m. and 75 c.m. in length, bent once at right-angles.

I have not obtained, however, a similar result with the emanations from hydrogen peroxide. As shown by Dr. Russell, this substance has a strong action on a sensitive photographic plate. The emanation from a bottle half full of hydrogen peroxide acts strongly on a sensitive film laid over the open mouth of the bottle for twenty-four hours, while there is no action in seventy-two hours if a U-shaped tube passed through the cork of the bottle and the sensitive film is put close to the open end of the tube. Dr. Russell tells me his observations confirm my experiments.

A highly active self-luminous radium compound loses some of its power on long exposure to the ordinary air of the laboratory. Ignition to red heat restores, however, its self-luminosity, and when sealed in a vacuum its activity remains as great as at first. When enclosed in glass the glass soon assumes a pink colour, which is not superficial, as already observed by M. and Mme. Curie. By immersing a section of the glass in a liquid of the same refracting power as itself, the colour is seen to penetrate below the surface. If, however, the radium compound is sealed *in vacuo* in a quartz tube no coloration takes place, and I can detect no diminution of energy even in twelve months.

Electrons from radium will pass through aluminium and a considerable length of air and affect a sensitive film.*

* Using an active compound of radium, I have obtained an impression on a sensitive film through a penny-piece,

Experiments on this point were tried with polonium, and it was found that air offered great obstruction.

Three shallow cells 17 m.m. in diameter and 2 m.m. deep were filled with polonium subnitrate, the same quantity in each cell, the surfaces being levelled. Over these cells were fixed three pieces of lead pipe of lengths of 1, 2, and 4 inches, so that each cell of polonium had its emanations confined to its own tube. Sensitive films were put over each tube, and the whole kept in total darkness for 144 hours. At the end of that stretch of time the films were developed. No image was seen on the film 4 inches from the polonium, a faint image was perceptible on the film 2 inches off, and a stronger one on the film 1 inch off. Measured in the opacity meter the figures were:—

Over 1 inch tube—Opacity log.=0.18; Opacity=1.51.

Over 2 inch tube—Opacity log.=0.04; Opacity=0.11.

A repetition of this experiment, using tubes of glass instead of lead, gave almost identical results.

The electron theory explains a fact which has long puzzled experimentalists. It is well known that if a coin is laid on a sensitive plate in perfect darkness and connected with one pole of an induction coil for a few seconds and then developed, an image can be obtained of the raised parts of the coin. This has generally been explained by saying that the electrified stream of air, or the "brush discharge," affects the film like light.

But Mr. F. Sandford (*Nature*, vol. lv., p. 485) shows that coins embedded in the centre of a block of paraffin 2 c.m. thick, where they could not send off streams of electrified air, can still be photographed by means of the induction coil. Under these circumstances it is probable that electrons are the agents, as electrons will easily pass through paraffin wax from the coin to the sensitive plate, when the coin is connected with the negative pole of an induction coil, the other pole being connected with a metal plate placed below the wax block.

Hitherto we have been dealing with negative electrons—a free positive electron at present is unknown. In a paper communicated to the Royal Society, December, 1900 (*Phil. Trans.*, A, 1901, vol. 196, p. 525), the Hon. R. J. Strutt offers a suggestion as to positive ions which in a satisfactory manner appears to explain much that hitherto has been left doubtful, not to say contradictory.

He adopts the generally recognised theory that the deflectable Becquerel rays consist of a stream of negative corpuscles with enormous velocities proceeding from the radio-active body. But there are two kinds of Becquerel rays, one deflectable and penetrating, the other non-deflectable and easily absorbable. Mr. Strutt considers that these non-deflectable rays are positive ions moving in a stream from the radio-active body.

He says:—"We know that the positive ions in gases carry the same charge as the negative, and that they have an enormously greater mass. Unless, therefore, their velocity is smaller out of all proportion than the negative ions, it is to be expected that they will be much less easily deflected by the magnet. . . . Next it may be noticed that the smaller penetrating power would be well accounted for by the size of the positive ions, which would, of course, make more collisions with the molecules of the surrounding gas than the much smaller negative ions."

Of the three radio-active bodies, radium, actinium, and polonium, actinium appears to emit corpuscles almost entirely of the penetrating, deflectable kind, polonium rays of the non-deflectable, non-penetrating kind, whilst radium emits rays of both kinds.

On the above hypothesis corpuscles from polonium might consist of the heavy positive ions; to test the accuracy of this inference experiments are now in progress.

Some curious and far-reaching inferences may be drawn from Mr. Strutt's view, supposing it to be correct, that positive as well as negative corpuscles will fly off from a radio-active body. In a paper "On Electrical Evaporation" (*Roy. Soc. Proc.*, June, 1891, vol. 1., p. 88) I showed that many bodies, such as silver, gold, platinum, &c.,

usually considered non-volatile at ordinary temperatures, easily volatilise in a vacuum if connected with the negative pole of an induction coil, remaining fixed when connected with the positive pole. This phenomenon was first observed by Dr. Wright, of Yale College, and was applied by him for the production of mirrors for physical apparatus. It is shown by experiments that the action in the vacuum tube is of two kinds. A silver pole was used, and near it, in front, was a sheet of mica with a hole in its centre. The vacuum was very high ($P=0.00068$ m.m.), and when the poles were connected with the coil, the silver being negative, electrons shot from it in all directions, and passing through the hole in the mica screen, formed a bright phosphorescent patch on the opposite side of the bulb. The action of the coil was continued for some hours, to volatilise a certain portion of the silver. On subsequent examination it was found that silver had been deposited only on the mica screen and in the immediate neighbourhood of the pole; the far end of the bulb, at the spot which had been glowing for hours from the impact of electrons, being free from silver deposit. Here then are two simultaneous actions. Electrons, or as I once called them "Radiant Matter," shot from the negative pole, and caused the glass against which they struck to glow with phosphorescent light. Simultaneously the heavy positive ions of silver, freed from their negative electrons, or under the influence of the electrical stress, likewise flew off, and were deposited in the metallic state near the pole.

An experiment was tried to discover if the ions of metal, deposited in this manner on a metal plate connected with an idle pole, in the full stream of + ions and - electrons, showed any special + or - electrification. In all cases the electrification was positive. This lends support to Mr. Strutt's view that + ions as well as - electrons will fly off from a radio-active body. Even these results, however, must not be taken as conclusive, for in a paper published in 1891 ("Electricity in Transitu: from Plenum to Vacuum," *Journ. Inst. Elect. Engin.*, vol. xx., p. 10), I showed that at a high vacuum nearly the whole of the interior of a tube through which an induction spark was passing was electrified positively, negative electrification being detected only in the immediate neighbourhood of the negative pole.

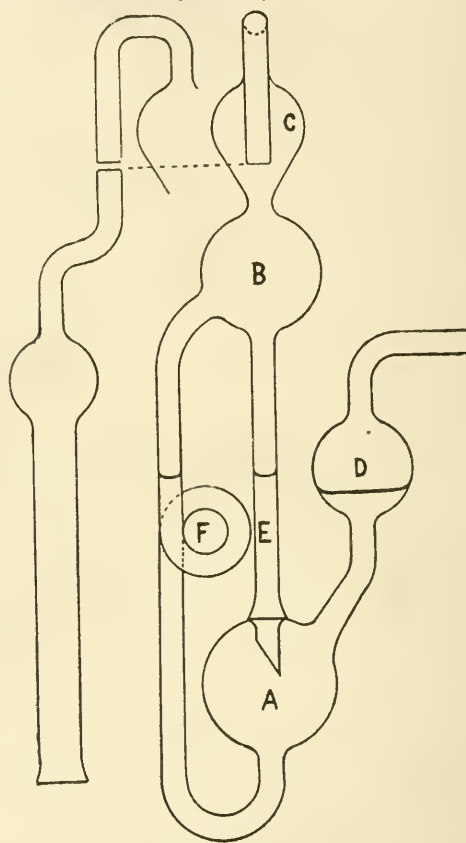
During the course of my experiments a curious circumstance was observed, which deserves record as it may elucidate some of these obscure phenomena. While the volatilisation of the silver pole is rapidly proceeding, the metal glows as if red-hot. This "red heat" is superficial only. The metal instantly assumes, or loses, the appearance of red heat the moment the current is turned on or off, showing that the high temperature does not penetrate below the surface. The volatilisation of the positive ions is confined to the surface, and the surface glow is connected with that action. If instead of silver, a good conductor of heat, I take diamond, a bad conductor, the surface layers are changed sufficiently to convert them into a form of graphite, which from its great resistance to oxidising agents, cannot be formed at a lower temperature than 3600°C .

Royal Institution.—On Tuesday next, March 11th, Professor E. B. Poulton, F.R.S., Hope Professor of Zoology in the University of Oxford, will deliver the first of a course of two lectures at the Royal Institution on "Recent Researches on Protective Resemblance, Warning Colours, and Mimicry in Insects"; and on Thursday, March 13th, Mr. E. T. Reed, of the staff of *Punch*, will commence a course of two lectures on "Caricature in and out of Parliament." The Friday Evening Discourse on Friday, March 14th, will be delivered by Professor Silvanus P. Thompson, his subject being "Magnetism in Transitu"; the succeeding discourse on March 21st will be given by Geheimrath Professor Otto N. Witt, of Berlin, on "Recent Developments in Colouring Matters" (in English). There will be no Evening Meetings on March 28th and April 4th.

A NEW DESIGN FOR POTASH BULBS.

By J. N. TERVET.

POTASH bulbs, whether made on the Liebig or on the Geissler pattern, have two disadvantages: first, the potash is not used up uniformly; secondly, crystallisation of potassium carbonate sometimes occurs and hinders the passage of the gas. To obviate these faults, I have designed bulbs, shown in the sketch, in which the current of gas itself causes the caustic potash to circulate through the whole apparatus. At the same time the mixture of gas and potash solution is so intimate that the speed of absorption is increased, and the time necessary to execute a combustion can be appreciably diminished.



(Two-thirds natural size).

It will be observed that the apparatus consists of four bulbs. The greater bulk of the potash is contained in A when not in use. The connection between the upper bulb, B, and the under bulb, A, is effected by the tube E, which is cut off obliquely at the lower extremity. In addition, connection is made by the syphon tube, F. C and D are safety bulbs.

The gas passing through D enters A and depresses the potash solution until the level reaches the oblique cut. The gas rises through E in a stream of small bubbles carrying the potash solution upward into B, from which it returns to the lower bulb, A, by means of the syphon tube, F.

The total weight of the apparatus when charged is 40 to 45 grms. The following analyses have been performed, using the apparatus:—

Dimethyl Fluoran.

0.1297 grm. substance gave 0.3829 grm. CO_2 , 0.0596 grm. H_2O .

	C.	H.
C ₂₂ H ₁₆ O ₃ requires	80'45	4'92
Found	80'51	5'15

Amyl Alcohol.

0'1200 grm. substance gave 0'2994 grm. CO₂, 0'1471 grm. H₂O.

	C.	H.
C ₅ H ₁₂ O requires.. ..	68'08	13'74
Found	68'04	13'74

Acetparabromanilide.

0'1782 grm. substance gave 0'2919 grm. CO₂, 0'0578 grm. H₂O.

	C.	H.
C ₈ H ₈ ONBr requires	44'84	3'77
Found	44'67	3'63

The apparatus may be obtained from the firm of Max Kaehler and Martini, Berlin.
East London Technical College.

A BIBLIOGRAPHY OF STEEL WORKS ANALYSIS.

PART XII.

By HARRY BREARLEY.

(Concluded from p. 103).

IRON.

III. VOLUMETRIC ESTIMATIONS (*continued*).

b. As Ferric Salts.—

1699. LANDOLT (*C. N.*, vi., 184).—Destroy free HCl with NaA, add excess hypo., and titrate with I and starch.
1700. CRAFTS (*C. N.*, xxviii., 44).—Evaporate HCl solution until the crust on the surface dissolves with difficulty; titrate with hypo.
1701. OUDEMANN (*C. N.*, xvi., 218; and xxii., 256).—To HCl solution add KCNS and titrate with hypo. Sr, Ca, Mg, Mn, Ni, Co, and Cu do not interfere.
1702. HASWELL (*J. I. S. I.*, 1883, 385).—Add soda salicylate in 1701; then hypo. till violet colour goes, and then K₂Cr₂O₇ till it reappears. See also OUDEMANN and HASWELL (*C. N.*, xlvii., 210) and BRUEL (*C. N.*, xlviii., 248).
1703. NORTON (*C. N.*, lxxx., 89).—Estimation with hypo. and I. Determines some necessary relations between acidity, dilution, &c.
1704. PSZCZOLKA (*C. N.*, xlvii., 107) and PARTHIEL (*J. I. S. I.*, 1890, i., 374).—Add KI to faintly acid ferric solution, and titrate with hypo. and starch.
1705. FALIERES (*J. C. S.*, xlviii., 1011) and NIHOUL (*C. N.*, lxxvii., 196).—Distil acidified Fe₂Cl₆ with KI, and titrate volatilised iodine.
1706. CARNEGIE (*C. N.*, lx., 87).—Investigates nature of reaction between Fe₂Cl₆ and KI, on which estimation of former depends.
1707. MORELLS (*J. S. C. I.*, 1884, 179).—Heat with KI, add a known amount of Hg, and shake. The free I and Hg combine and the Fe is deduced from the loss of Hg on re-weighing.
1708. WINKLER (*C. N.*, xxi., 233).—Add KCNS and then CuCl until the colour disappears and a cloud of CuCNS is formed. Co, Ni, Cu, and As do not interfere. See also GIBBS (*C. N.*, xvii., 161).
1709. WEIL (*C. N.*, xlvi., 284) and JEAN (*J. C. S.*, lxiv., ii., 492).—Add SnCl₂ to HCl solution of Fe₂Cl₆ until colour goes; or add CuCl₂ to heighten end-reaction.
1710. HEMPEL (*C. N.*, lii., 321).—Ignite with Na₂CO₃+CaCO₃ to eliminate organic matter, dissolve in HCl, and titrate with SnCl₂.

1711. MAHON (*J. S. C. I.*, 1893, 1061).—SnCl₂ is added to a solution containing HgCl₂ and a little PtCl₃; a faint excess precipitates a dark cloud of finely-divided Hg and Pt.
1712. MORAHT (*C. N.*, lxx., 275).—Add ferrocyanide until the sulphocyanide colour, kept in solution with ether, is dispersed.
1713. CHARPENTIER (*C. N.*, xxviii., 71).—To solution containing no free acid add KCNS and titrate with caustic alkali. A like process was suggested by ROSS (*C. N.*, xvii., 23 and 35) and adversely criticised by WRIGHT.
1714. PURGOTTI (*J. S. C. I.*, lxxii., ii., 77).—An acid solution of the blue oxide (Mo₃O₈) mixed with hot Fe₂O₃ solutions is quantitatively decolorised.
1715. JUETTE (*C. N.*, xvii., 63).—The amount of tartaric acid needed to retain iron (Cr, Mn, Al) in solution is proportional to the amount of the latter.
1716. CARNOT (*J. S. C. I.*, 1889, 138).—Cold acid FeO solutions are more effectually oxidised by H₂O₂ than by any other reagent.

IV. COLORIMETRIC ESTIMATIONS.

1717. DAVIES (*C. N.*, viii., 163).—Add KCNS, and compare with standard.
1718. SKEY (*C. N.*, xvi., 180 and 233).—When the mixed Fe₂Cl₆ and KCNS is treated with excess HCl, Fe is volatilised at ordinary temperatures.
1719. KRÜSS and MORAHT (*C. N.*, lxiv., 255).—The KCNS colour is due to the formation of Fe(CNS)₃. 9KCNS+4H₂O.
1720. LUNGE (*C. N.*, lxxiii., 250).—Shakes out the KCNS colour with ether. Better to oxidise Fe with KClO₃ than with HNO₃.
1721. WEBER (*C. N.*, xlvii., 165).—Chlorides of the alkaline earths retard or may prevent the KCNS reaction.
1722. THOMSON (*C. N.*, li., 259).—Ag, Cu, Co, and HgCl₂ interfere with the KCNS colour.
1723. TATLOCK (*J. S. C. I.*, 1887, 276).—Influence of reagents, free acid, oxidisers, &c., on the KCNS colour.
1724. VERNON (*C. N.*, lxvi., 177, &c.).—Influence of temperature, dilution, acidity, &c., on the KCNS test. See also GLADSTONE (*C. N.*, lxvii., 1 and 66); ANDREWS (*C. N.*, lxx., 165); KRÜSS and MORAHT (*C. N.*, lxvi., 198); and RIBAN (*J. S. C. I.*, 1892, 269).
1725. SABANEFF (*J. C. S.*, liv., 757).—Colour of Am₂S solutions used.
1726. JOB (*J. C. S.*, lxxvi., ii., 51).—Fe₂S dissolved in soda pyrophosphate gives a green solution well adapted to a colorimetric estimation of Fe.
1727. CARNELLEY (*C. N.*, xxx., 257).—The blue colour formed by ferrocyanide can detect 1 part Fe in 13,000,000 of water. Process elaborated for estimation of Fe in water.
1728. WAGNER (*C. N.*, xlv., 35).—Limit of sensitiveness of some reactions for Fe and Cu.

V. MISCELLANEOUS.

1729. JULIEN (*C. N.*, xxiv., 292), BLAIR (*C. N.*, lvi., 183), and MORGAN (*J. S. C. I.*, 1894, 1023).—Schemes for elaborate analysis of iron ores.
1730. BETTEL (*C. N.*, xliii., 100).—Discusses the determination of basic cinder and oxides in iron, and reviews a number of methods proposed for this purpose. The following (not exhaustive) references are to papers dealing with the estimation of oxides or slag:—GLADKY (*J. C. S.*, lxiv., ii., 388); PARRY and MORGAN (*C. N.*, lxvii., 260); LEDEBUR (*J. S. C. I.*, 1882, 366); SCHNEIDER (*J. S. C. I.*, 1900, 693); TUCKER (*J. I. S. I.*, 1881, 205).
1731. FOEHR (*C. N.*, xlvi., 40).—Ores containing MnO₂ need prolonged boiling to expel the Cl formed, and Fe₂Cl₆ is volatile even at 50°.

1732. FRESenius (C. N., xvi., 37) and TALBOT (C. N., lxxv., 227).— Fe_2Cl_6 is not volatilised on boiling with acids.
1733. BORNRÄGER (Z. C. S., lxx., ii., 502; and lxxviii., ii., 171).—Ignited Fe_2O_3 dissolves instantly if metallic iron is also being dissolved in the HCl , or if a little MnO_2 is added.
1734. ANON. (C. N., xxxviii., 11).—Ignited Fe_2O_3 can be dissolved in HCl after boiling to flocculent condition with KHO .
1735. ZIRNITE (Z. I. S. I., 1888, i., 368).—A 30 per cent NaHO solution dissolves Fe_2O_3 as NaFeO_4 ; it is re-precipitated on diluting or standing.
1736. JEANNEL (C. N., xvii., 286).—Properties of "neutralised" ferric chloride [$\text{Fe}_2\text{Cl}_6 \cdot 9\text{Fe}_2(\text{HO})_6$] solutions.
1737. WARREN (C. N., lxxii., 100).—Au and Ag were estimated in iron by making the sample ($\frac{1}{4}$ lbs.) the + pole of an acid battery. The C residue and a little Fe were mixed with litharge, cupelled, &c.
1738. WARREN (C. N., lxxv., 91).—Samples which have been in contact with a borax flux contain B up to 2 per cent.
1739. WIBORGH (C. N., lxxviii., 4).—Determines the reducibility of Fe ores. The reduced Fe is estimated by measuring the H evolved on treating with acids.
1740. MEUNIER (C. N., xix., 5).—Immediate analysis of meteoric iron.
1741. LEDEBUR (Z. I. S. I., 1894, ii., 483).—Uses the ether method to separate iron from Cu, Sb, As, Pb, Cr, V, Mn, Ni, Co, and Ti existing in steel.
1742. J. T. (C. N., lxxix., 157).—Insoluble specular ores are mixed with asbestos filter-paper and ignited; they are then soluble in HCl .
1743. BECHAMP and SAINTPIERRE (C. N., iv., 316).—Metallic Pt reduces HCl solutions of Fe_2Cl_6 , and is itself dissolved thereby.
1744. DUDLEY (C. N., lxxv., 257).—"Some Present Possibilities in the Analysis of Iron and Steel."

ON THE AGRICULTURAL VALUE OF THE NITROGEN OF THE BLACK MATTER IN PYRENEAN PHOSPHATES.

By JULES JOFFRE.

It has long been known that many organic materials, although containing nitrogen, have not the slightest beneficial action on vegetation. Boussingault made the remark that coal, though containing nitrogen in the organic state, did not cause, in spite of that, any chemical action favourable to the growth of plants.

In recent years considerable deposits of phosphates have been found in the Pyrenees containing a black nitrogenised organic substance. It seemed to me to be of interest to ascertain what is the agricultural value of this substance.

For this purpose I have carried out two series of experiments laid down on the same lines as those of which I have already published a description, taking as bases of comparison, on the one hand, nitrate of soda, sulphate of ammonium, and dried blood; and on the other hand, coal. In each pot I put the same amount of nitrogen in these different forms. The sample of Pyrenean phosphate on which I experimented contained 0.14 per cent of nitrogen. Naturally, I added some insoluble phosphate to equalise the relatively high proportion that the Pyrenean phosphate contained. Further, in all the pots I put sufficient quantities of potash, lime, magnesia, and soluble phosphoric acid.

Under these conditions the nitrated organic matter of the Pyrenean phosphate behaved in the same manner as the coal. It did not cause the slightest augmentation of

weight of the plants submitted to its action. On the other hand, the nitrate of soda, the sulphate of ammonium, and the dried blood produced a considerable increase of the crop.

The result of these experiments does not in any way diminish the importance and great future which M. David Levat attributes to the deposits of this Pyrenean phosphate; the more so as the amount of nitrogen contained always being small could not have much influence on the final value of this material. Still it appeared to me to be of use to publish my experiments so that agriculturalists might not be mistaken in the value of the nitrogen present in this material.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 22.

ON THE ESTIMATION OF TIN BY LENSSEN'S PROCESS.

By J. A. MULLER.

THE volumetric estimation of tin by means of an iodine solution is frequently used in laboratories on account of the rapidity with which the operation can be performed and the sharpness of the end of the reaction of the iodine on the tin in alkaline stannous combination.

This estimation—as far as we can judge from the figures quoted later on—gives, as a rule, however, rather too low results, even when taking every precaution to prevent the oxidation of the stannous solutions, as much during the solution of the metallic mass in hydrochloric acid as during the titration.

With the object of checking Lenssen's method I commenced by preparing pure iodine by submitting commercial doubly-sublimed iodine to five more successive sublimations. To obtain any determined weight of this metalloid a quantity, weighed approximately, was rapidly transferred to a ground glass stoppered weighing bottle by means of a funnel; the stopper should be slightly smeared with vaseline, and the whole previously tared; the stopper must be inserted immediately, and the bottle placed on the balance. The iodine was then dissolved in the same bottle, taking care not to lose any of the vapour, by means of a concentrated solution of pure iodide of potassium, obtained by evaporating a perfectly clear alcoholic solution of this salt *in vacuo*. The solution of iodine was then diluted to a known volume with cold, boiled, distilled water.

The tin used for these experiments gave me the following centesimal results by gravimetric estimation:—

Sn	99.76
Fe	0.13
Pb	0.05

99.94

For the purpose of titrating, this metal was dissolved in pure, concentrated hydrochloric acid (10 c.c.). The solution was effected in a test-tube kept in an inclined position, and fitted with an indiarubber stopper through which passed a curved tube, the end of which was plunged into a small flask containing a little water. Only a very moderate heat is required, and as soon as the solution is complete the contents of the test-tube are run off, and the tube rinsed—with cold, boiled, distilled water—into a large conical beaker full of carbonic anhydride. We then add 80 c.c. of a 10 per cent solution of Seignette salt prepared with boiled water; then, at several intervals, enough carbonate of soda, in powder, to make the solution distinctly alkaline, taking good care to incline the beaker so as to prevent any loss by projections. Finally, into the limpid solution we slowly run, by means of a pipette and with constant stirring, a volume of iodine solution, almost sufficient to produce total oxidation; then, after the addition of a little starch emulsion, the titration is finished with the help of a burette.

A blank experiment, made under the same conditions, gave a solution which one drop of iodine liquor coloured blue; on the other hand, by adding to 80 c.c. of the solution of Seignette salt 5 c.c. of a solution of stannous chloride titrating 1.3 c.c. of iodine, and then titrating after about an hour, after the addition of carbonate of soda, I re-obtained an iodine value of 1.28 c.c.; the medium with which the stannous chloride was mixed, after the solution of the tin, was thus neither reducing nor oxidising.

All the weighings and gauging of the vessels used for measuring the volumes were carried out by means of the same certified weights.

The following are the results obtained:—

Weight of tin dissolved.	Volume of iodine liquor used.	Decinormal coefficient of the liquor.*	Corresponding weight of tin.	Weight of tin.
Grm.	C.c.		Grm.	Per cent.
0.5286	88.66	0.9930	0.5216	98.68
0.4609	77.23	0.9940	0.4549	98.69
0.4131	69.23	0.9940	0.4077	98.70
0.4529	75.07	1.0108	0.4496	99.27
0.4054	67.24	1.0108	0.4027	99.34
0.6009	99.36	1.0108	0.5951	99.03
0.6329	104.64	1.0108	0.6267	99.02
1.6304	99.77	1.0595	0.6263	99.35

* In these experiments we took the figure 126.85 as the atomic weight of iodine, and 118.5 as that of tin. One c.c. of decinormal iodine liquor thus corresponded to 0.005925 gm. of tin.

As the tin used might have contained a little tungsten, which is difficult to detect directly, I treated a certain quantity with nitric acid, then after washing and drying I reduced the residue by means of cyanide of potassium. By operating with the pure tin thus obtained, in the same way as with the tin containing 99.76 Sn and 0.13 Fe used in the preceding experiments, the titration gave 99.31 and 99.24 instead of 100.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 23.

ON PYRITE AND MARCASITE.*

By H. N. STOKES.

(Continued from p. 93).

IX. FORM OF OCCURRENCE OF COPPER IN COPPER-BEARING PYRITES.

THE problem of determining whether a given specimen of cupriferous pyrite contains its copper in the form of chalcopyrite or chalcocite was suggested by a geologist, and the following shows that such determination is possible when marcasite or other sulphides are not present in considerable quantities.

Oxidation Experiments.

Mixtures of pyrite with chalcopyrite, chalcocite, and bornite were prepared, each containing 3 per cent copper. For chalcopyrite and chalcocite these mixtures have the following composition:—

Pyrite	91.33	or	{ Cu	3.00
Chalcopyrite ..	8.67		{ Fe	45.20
			{ S	51.80
Pyrite	96.24	or	{ Cu	3.00
Chalcocite ..	3.76		{ Fe	44.85
			{ S	52.15

The bornite mixture has an intermediate composition. It would be scarcely possible to distinguish these by ordinary analytical methods, especially in the presence of small amounts of impurity. The values of p were found to be—

Pyrite-chalcopyrite	62.7
Pyrite-chalcocite	75.9
Pyrite-bornite	76.4

* From the *Bulletin of the U.S. Geological Survey*, No. 186.

It appears that the oxidation method does not admit of distinguishing chalcocite and bornite with certainty in a pyrite with 3 per cent copper, but that these may be readily distinguished from chalcopyrite even when the copper is considerably less than 3 per cent. It can also be determined with some probability whether a mixture of chalcopyrite with the other sulphides of copper is present. In the present case the figures given by chalcocite or bornite and chalcopyrite differ by more than thirteen times the probable error of a determination.

This method will probably be of value in synthetic studies of copper ores. It is thus made possible, for example, to ascertain whether the first action of a cupric salt on pyrite is to produce chalcopyrite alone or a mixture of this with the other sulphides, without having to wait for the slow process of crystallisation to produce the minerals in a form in which they can be recognised under the microscope. By employing fine powders the rapidity of the change will be vastly increased, while the net results, according to the mass law, will be the same.

Detection of Chalcopyrite in Pyrite or Marcasite and in Rocks.

Chalcopyrite mixed with pyrite or marcasite may be readily detected, if not in too small amount or too finely divided, by exposing the sample to bromine vapour for half a minute, and then to hydrogen sulphide gas; the chalcopyrite is blackened, while the iron sulphides remain bright. Particles of chalcopyrite which would otherwise be overlooked are thus easily detected and their outlines sharply defined. I have used the same procedure to detect and establish the nature of minute grains of chalcopyrite enclosed in rocks.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 28th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

A PAPER on "Focal Lines and Anchor-ring Wave-fronts" was read by Prof. J. D. EVERETT.

When a small cone of rays is obliquely incident on a spherical reflecting or refracting surface, the rays after reflection or refraction no longer compose a true cone. Instead of meeting in a point they form a narrow neck, and this neck is flattened in two places, called the *two focal points*, the planes of flattening being at right angles to each other. Optical writers give the name *focal lines* to the sections of the pencil made at the focal points by planes perpendicular to the axis of the pencil; but it would be more appropriate to give the name to the sections which most nearly resemble lines, whatever angle they make with the axis of the pencil. Attention is drawn in the present paper to the case in which the wave-front in one of its positions is a *tore* (or anchor-ring). Even when dealing with wide angled pencils there are then two well-defined focal lines, the primary focal line being what may be called the circular axis of the *tore*, and the secondary a portion of the line about which the generating circle turns to form the anchor-ring. Toric wave-fronts can be produced by reflection from a mirror made by allowing an ellipse or portion of an ellipse to revolve completely round an ordinate erected at one focus, and employing it to reflect rays diverging from a small source at the other focus. The primary line is always real; the secondary is real or virtual according to the position of the area of incidence of the pencil.

Mr. R. J. SOWTER pointed out that when a thin oblique pencil, or small cone of rays, is reflected or refracted by a

spherical surface, the pencil rays form a narrow neck, and that this neck is flattened in two places called the *focal lines* and not the *focal points*; and that the focal lines cut the principal ray or axis of the pencil in the focal points. In the case of thin pencils the focal lines are elementary, and may be considered as straight lines, and an infinite number of planes can pass through them or contain them. This leads to the mutually rectangular primary and secondary planes of the pencil being selected. But if the elementary focal line is considered curved, as it is in general, only one containing plane can be chosen, namely, the plane of the curve. Real or physical focal lines are not in planes related with the focal points as suggested by Prof. Everett. It was also pointed out that the criterion for anchor-ring or toric waves is that the focal lines are respectively a circle and a straight line perpendicular to the plane of the circle and lying in its axis, and that a toric wave-front could be formed by the refraction of a hollow cone of light at an annular ring on a spherical surface. The wave-front in the refracting medium is then toric; that is, it is a circular trough which is part of an anchor-ring. The primary focal line is a circle and the secondary a straight line of limited length.

The CHAIRMAN said that optical writers often used the term focal lines to denote the sections of the wave surface made by two mutually perpendicular planes through the focal points.

A paper entitled "*Contributions to the Theory of the Resolving Power of Objectives*" was read by Prof. EVERETT.

The practical limit to the resolving power of objectives depends upon the blurring due to diffraction. Observations on double stars for the purpose of investigating the separating power of telescopes have been made by Dawes, who arrived at the conclusion that the angular distance between the two components, when they are nearly equal in magnitude and are just separated, is given by the formula, 4.56 seconds divided by the diameter of the objective in inches. Foucault also investigated the matter experimentally, and in 1830 Airy calculated the brightness at various points of the spot and rings which constitute the image of a point source formed by an objective. If the extreme difference of optical path for disturbances coming from different points of a concave wave-front to a point at lateral distance b from the geometric focus is made equal to the wave-length of light, a value for b is obtained which represents with fair accuracy the limit of separation as determined by experiment. The formula agrees with that of Dawes if $\lambda = 0.56$ micron., whereas the wave-length of the brightest ray is usually taken as 0.55 micron. In the case of microscopes the author has supposed that the formula for the minimum distance b still holds good, and combining this equation with the sine condition applicable to optical systems giving sharp flat images, he has deduced the expression which has been extensively used for the distance between lines or points which can be barely separated. Microscopic test objects are not self-luminous, like double stars, but are viewed by transmitted light. If no condensing arrangement is employed, the pencil of light sent by a point of the object to the objective consists, in effect, of rays from different sources. The result of this is that the image of the point is larger and more blurred. The cure for this evil is furnished by employing a condenser of high quality, to throw upon the part of the object under examination a very sharp image of the source of illumination. Each point of the object thus gets its light from its own special point of the source; the object, therefore, acts as if it were self-luminous, and the power of the instrument is increased. The benefit derived from sharp focussing on the object explains the advantage of using an achromatic condenser, and not, as formerly recommended by Abbe, one which is not achromatic. Another advantage of sharp focussing by the condenser is that there can be no interference of the light from different parts of

the object. The author then gives an explanation of the advantage of oblique illumination, and arrives at the view of microscopists that the obliquity of illumination should be rather less than the obliquity of the extreme rays of the incident pencil. The paper concludes with Hockin's proof of the sine-condition.

The CHAIRMAN expressed his interest in the paper, and referred to the rational reason given for the use of an achromatic condenser.

A paper on "*The Absorption, Dispersion, and Surface Colour of Selenium*," by Prof. R. W. WOOD, was read by the SECRETARY.

The dispersion of selenium has been investigated by means of prisms made in the same manner as the cyanine prisms already described by the author. The substance is much more transparent than cyanine, and prism angles of four or five degrees can be employed. Determinations were made with three selected prisms down to wave-length 61 ; below this the interferometer method was employed. Uniform films of selenium were obtained on plates of plane parallel glass, by means of a flat selenium cathode in a high vacuum, and the displacements of the interference fringes by the introduction of the films were measured for lights of different known wave-lengths. Wedge-shaped films were then employed which allowed the displacement for any wave-length to be measured for the maximum thickness capable of transmitting the light. An advantage of the wedge-shaped films is that the fringes are curved, and the displaced fringe can be easily identified with the undisplaced. The refractive indices obtained in the red by prisms were used as a basis for the calculation of the indices in the rest of the spectrum from the interferometer measurements. Determinations were made in this way down to wave-length 40 , beyond which it was impossible to go owing to the powerful absorption. A curve has been plotted showing the relation between refractive index and wave-length. It has a maximum at wave-length 50 (0.00005 c.m.) where the refractive index is 3.13 . An examination of the light transmitted by a thin film showed that there was no return of transparency in the ultra-violet, at least down to wave-length 28 . Photometric measurements were made of the transmitted light, both visible and ultra-violet, and a curve has been drawn with wave-lengths as abscissæ, and extinction coefficients as ordinates. It is proved that the extinction coefficient increases continuously with decrease in wave-length as far as wave-length 22 , where the coefficient has as high a value as in the case of metals. The author concludes that the absorption is due, not to a single band, but to a series of overlapping bands. The object of this work was to determine whether there was a return to partial transparency in the ultra-violet region. This question appears to be answered in the negative although a possible turning point in the curve might be masked by the reflection coefficient of selenium. The high value of the extinction coefficient in the ultra-violet led the author to look for traces of selective reflection in this region. The light of an arc lamp was reflected successively from six surfaces of selenium, and the image of the crater after the sixth reflection, although faint, was without colour or excess of ultra-violet light. If the data obtained in the paper for refractive index and extinction are used in the formula for reflection from an absorbing medium a result is arrived at which indicates that the reflection increases rapidly with decreasing wave-length. As multiple reflections from selenium surfaces give no trace of colour, errors must exist in either the refraction or the extinction curve. The author suggests that in the case of films of thickness less than the wave-length of light, the displacement of the interference fringes does not give a measure of the refractive index.

The CHAIRMAN exhibited some Tellurium Mirrors made in the same way as the selenium ones used by Prof. Wood.

The Society then adjourned until March 14th.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Ordinary Meeting, February 18, 1902.

Mr. CHARLES BAILEY, President, in the Chair.

MR. R. L. TAYLOR read a paper "*On a Modification of Rose's Method of Separating Cobalt and Nickel.*"

In the original process described by Rose and improved by T. H. Henry, barium carbonate and chlorine (or bromine) were added to rather strongly acid dilute solutions of the two metals, and allowed to stand, with frequent shaking, for from twelve to eighteen hours. The cobalt was precipitated as sesquioxide, while the nickel remained in solution. Mr. Taylor finds that if a neutral solution is used the precipitation of the cobalt is complete in a few minutes, and that excellent quantitative results can be obtained. The retardation of the reaction which occurs when the solution is (as Rose and Henry used it) strongly acid at the outset, the author shows, is due to the free carbonic acid which is produced in the solution when the carbonate is added to the acid liquid. A similar retardation occurs in a neutral solution if carbon dioxide is first bubbled through it or if soda-water is added to it. Mr. Taylor recommends the process for the separation and detection of cobalt and nickel in the ordinary process of qualitative analysis. Either barium or calcium carbonate may be used (dry precipitated, as usually sold, will do) with bromine-water, and if no free acid is present at the outset the cobalt is all precipitated in five minutes. On filtering, nickel can be readily detected in the filtrate by adding a little ammonia and ammonium sulphide. If there is any free acid present at the outset, it must either be boiled away or neutralised before adding the carbonate. Sodium carbonate may be used for neutralising, but then the free carbonic acid must all be boiled away, and the liquid cooled before adding the carbonate and bromine water.

MR. D. L. CHAPMAN described some experiments which have been carried out, in conjunction with Mr. F. A. LIDBURY, principally for the purpose of discovering whether Faraday's law may be considered as applying to gases.

The electric discharge was passed through water vapour, and the separation of oxygen and hydrogen which took place was found to be from two to three times as great as that which occurred in a voltameter placed in the same circuit. The results are therefore inconsistent with the view that the phenomenon is essentially electrolytic.

and the oxidases, as well as of panary fermentation and the fermentation of molasses.

The classification of soluble ferments adopted by the French author is based on their chemical behaviour, and is as follows:—I. The soluble hydrating ferments. II. The soluble oxidising ferments. III. The ferments causing molecular decomposition. Class I. embraces the soluble ferments of (a) carbohydrates (the subject of the present volume), (b) glucosides, (c) fatty substances, (d) proteins, (e) urea. Classes II. and III. are more briefly treated owing to less extensive knowledge. In discussing nomenclature M. Effront expresses regret that the rational system suggested by Duclaux has not been more universally adopted, for although it was not all that could be desired, it would have prevented confusion. He decides to use the names generally met in the literature of the subject.

In writing of the industrial applications of the soluble ferments the influence of French methods is naturally prominent; this appears in the chapter on panary fermentation, which, though scientifically accurate, does not entirely harmonise with American practice, nor with English processes that have not been affected by the customs of their friends across the Channel.

A valuable feature of the book is the bibliography annexed to each chapter, which, however, refers to journal literature not later than 1898; in a second edition the translator might well extend this bibliography to a more recent date.

There is a rather brief index.

H.C.B.

Elementary Chemical Theory. By G. H. MARTIN, M.A., F.C.S., Assistant Master at Bradford Grammar School. New Edition, Revised. London: Rivingtons. 1902. Pp. 24.

As its title indicates, this book is purely elementary, and is evidently intended for the use of young beginners. It begins with a definition of matter, which is described as anything having weight. Dalton's atomic theory is next explained, followed by Gay-Lussac's and Avogadro's laws. Next we come to symbols, formulæ, and molecular weights and valency, all taken seriatim. Part II. describes the different kinds of elements—metals and non-metals—bases and acids, nomenclature and equivalent, or combining weights, &c. The book appears to be well adapted to the needs of school-boys; it touches not only on elementary chemistry, but also on elementary physics, both of which are treated in a clear and concise manner; it is interleaved with blank pages to enable the student to make his own notes and observations, as his fancy takes him, and is indexed.

NOTICES OF BOOKS.

Enzymes and their Applications. By JEAN EFFRONT. English Translation by SAMUEL C. PRESCOTT. Vol. I., "The Enzymes of the Carbohydrates; the Oxidases." New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1902. Pp. xii. 322. 8vo.

THE number of treatises on soluble ferments in the English language is comparatively small, and makes this translation of Professor Effront's standard volume the more highly appreciated by students of bio-chemistry. In its English dress the original has been presented in the form in which it came from the pen of the author without additions or changes; it is actually a summary of the course given at the Institute of Fermentations of the new University of Brussels, and is designed both for students of pure science and for those particularly occupied in fermentation studies.

In successive chapters the author treats of the general properties of enzymes, of the action of diastases, of the individuality and classification of enzymes, of sucrase, amylases, maltase and its industrial applications, zymase,

Year-Book of the United States Department of Agriculture, 1900. Washington: Government Printing Office. 1901. Pp. 880.

THIS volume contains, besides the report of the secretary and the appendix, thirty-one articles; that is, five more than last year. With one exception every article was prepared by an employé of the department, and each division of original work is represented by one or more articles, each one covering some important line of work carried on. Thus the year-book for 1900 differs from some of its predecessors, which were devoted more especially to a review of the work of the several departments.

The illustrations, which are very well executed, comprise eighty-seven plates, nine of which are coloured, and eighty-eight figures in the text.

The work done, in a long life devoted to agriculture, horticulture, and kindred interests by the late Mr. William Saunders, is the subject of a brief notice by the editor, which fully justifies the prominent place given to his memory in this edition.

In the appendix, which it is desired to make an indispensable book of reference to the farmer, the agricultural

directory feature, introduced in 1899, has been continued; it has also been revised and corrected up to March 1st, 1901.

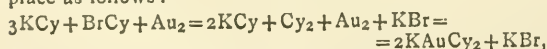
The statistics of farm crops, supplied as usual by the Statistician of the Department, have been re-arranged so as to present together the facts and figures relating to each crop, thus affording one complete view of results for a particular crop for the year. This change will be found, it is believed, especially convenient to farmers who have occasion to consult these figures in planning their future operations.

Cyanide Practice. By ALFRED JAMES, Mining and Metallurgical Engineer, Member of the Institution of Mining and Metallurgy, F.R.G.S., F.C.S., &c., Late Technical Manager and Special Expert in South Africa, New Zealand, Australia, United States, and elsewhere of the Company introducing the Cyanide Process. London: E. and F. N. Spon, Limited. New York: *Engineering and Mining Journal* (Incorporated). 1902. Pp. 164.

WHILE the same general principles govern the employment of cyanide for the extraction of gold from its ores, it must be remembered that modifications are numerous, and that new details of practical working are constantly coming into being. Possibly the most remarkable tribute to the efficiency of the cyanide process is the practical relegation to the back-ground of the numerous processes which formerly reappeared so persistently under new names, and in the hands of different inventors, all claiming the highest possible extractions at a minimum of cost.

A great deal of technical skill is necessary for the proper working of the cyanide process, there being many reasons why the extractions may be poor; for instance, soluble sulphides may be formed, the gold may be too coarse or in the form of telluride; again, base metals may be present, and these enter into combination with the cyanide and consume it. For the treatment of sulphide ores bromo-cyanide may be added, or the metallic sulphides may be eliminated by fine grinding, and the addition of a freshly precipitated lead salt, such as the chloride or carbonate, to decompose any soluble sulphide as soon as it is formed. In all cases of heavy consumption of cyanide it is as well to analyse the solution, and to determine the amount of cyanide accounted for by the metals in solution. Ores high in silver will naturally consume a good deal of cyanide. The author has met with gold-silver ores, not concentrates, for which 6 lbs. of cyanide have been required per ton of ore treated, merely to account for the silver in solution. Having found the amount of metals in solution, if the copper be multiplied by 3, the iron by 7, the silver by 1.2, and the gold by 0.7, the consumption due to each metal can be determined; if there is still any considerable balance, it may be due to the presence of acid salts in the ore, or in the water used.

The most important recent improvement in the cyanide process is the introduction of bromo-cyanide. The addition of bromo-cyanide to the ordinary cyanide solution in the proportion of not more than one part of the former to four of the latter, considerably accelerates the rate of solution of the gold, though it may not affect the final percentage of extraction; its addition, however, generally causes a greater consumption of cyanogen. Bromo-cyanide *per se*, that is, apart from its reactions in the presence of cyanide of potassium, can scarcely be claimed as a solvent of the precious metals. Indeed, as the author points out, it is remarkably stable until added to the cyanide solution, but if in addition gold is also present a reaction will take place as follows:—



and it is undoubtedly due to this reaction that the extensive use of bromo-cyanide is due, whether as an accelerator or as an aid to actual solution. The author also shows

that the presence of air is not only unnecessary for the solution of gold in the presence of bromo-cyanide, but that its addition causes no improvement in the extraction; on the other hand, when ferri-cyanide is being used the improvement shown by the addition of air is most marked.

We strongly recommend this book to the notice of any of our readers who are interested in gold extraction; it is exceedingly well written, and quite up-to-date; it is adorned with twenty-five illustrations, most of them being photographs of actual cyanide plants in operation in various parts of the world. The table of contents is full and comprehensive, but there is unfortunately no index. Possibly this omission may be remedied in a future edition.

CORRESPONDENCE.

CHEMICAL NOMENCLATURE.

To the Editor of the Chemical News.

SIR,—As I see two letters in your issue of December 6th last on the subject of chemical nomenclature sent from America I feel encouraged to write to you, as, although the idea of doing so on various matters has often occurred to me, I have felt myself so far away that it appeared useless.

My greatest difficulty in memory is in the names of persons, and therefore I quite agree with your correspondent E. Booth, that it would be advisable to drop the names of propounders of theories or laws and state instead what they refer to. I have seen examination papers in which such names have been used, in which, although I could state all the laws, &c., I could not connect them with the personal name, and so would probably have been plucked so far as these were concerned. Such questions are not an examination in pure chemistry, but to a large degree in verbal memory.

There is, however, even a worse evil continually growing, especially in communications from public analysts, of indicating processes, reagents, apparatus, &c., by the names of the proposers; thus tending to convert the chemistry of the analyst into the jargon of a trade line, the dog Latin, and trade marks of the pharmacist. I have a small French book, "*Répertoire des Réactifs Speciaux*," by F. Jean and C. Mercier, giving a description of some hundreds of these, but one finds many more, and they are growing every day. It is quite as easy to say of the determination of nitrogen, the soda-lime process, as Varrentrapp and Will's process, or sulphurous acid process, as Kjeldahl's process. It may be objected that a little more space would be occupied, but it is found that the same writers do not save words. Thus I noticed to-day that one writer suggested doing something "by means of" a platinum wire, when "with" would have been better—nine letters used instead of four.

Another expression to be condemned is the continual use of the words estimate or estimation, in connection with chemical work; they being used as if synonymous with determined or determination, conveying to outsiders an idea of laxity and approximate guess-work; as an estimation is only a probable guess at a number formed from imperfect data, whilst a determination is the result of actual weighing, measuring, or counting; subject, of course, in each case to errors arising from personal equation, &c., which are, or should be, reduced to the lowest possible limits. The Chancellor of the Exchequer estimates the revenue and expenditure of the coming year, but the determinations only come at the end of the time, and may be much over or under the estimates. An architect estimates the cost of a house, various builders do the same, and are prepared to contract for its erection, but these generally differ widely; the determination is found when the house is finished and the bill is presented. Some years ago I

had a case in point where a quartz reef was worked for gold, the average of all assays of the stone not differing much, being $3\frac{1}{2}$ ozs. per ton; but the gold recovered in the battery, and from the pyrites saved, was only $1\frac{1}{2}$ ozs. I suggested that the gold was lost in the pyrites, but was told all was saved. The directors, under my advice, got samples taken systematically of the sand from the battery containing the pyrites. The battery manager estimated that the stone contained $2\frac{1}{2}$ per cent of pyrites, and he saved that quantity; the determination of the pyrites gave 23 per cent. His estimate was based on the yield he had got from previous similar stone.—I am, &c.,

WILL. A. DIXON, F.I.C., F.C.S.

Chemical and Assay Laboratory,
97, Pitt Street, Sydney.

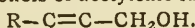
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

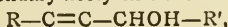
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiv., No. 6, February 10, 1902.

Crystallisation of Chromium Sesquioxide.—Alfred Ditte.—When potassium bichromate is heated to bright redness with common salt, and the mass when cool is treated with water, chromium sesquioxide remains crystallised in thin brilliant oily plates. The author experiments on the reason of this phenomenon and finds (1) that the crystallisation of the chromium oxide is not due to its solubility in the fused alkaline chloride, and (2) that the sodium salt is apparently very favourable to crystallisation, whilst the potassium salt seems to hinder it. Further experiments show that the phenomenon is really due to the formation of an oxychloride of chromium, CrO_2Cl_2 , and its combination with the halogen sodium salts.

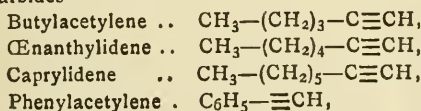
Condensation of the True Acetylenic Carbides with Aldehydes; Synthesis of Secondary Alcohols containing an Acetylenic Function.—Ch. Moureu and H. Desmots.—The authors recently discovered, whilst examining the condensation of the true acetylenic carbides with formic aldehyde, a very simple method of synthesising primary alcohols of acetylenic function—



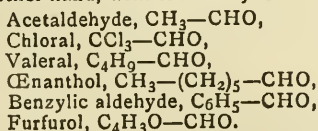
An extension of this method to other aldehydes led to the synthesis of secondary acetylenic alcohols—



a group of compounds totally unknown up to the present. The experiments were performed on the one hand with four carbides—



and, on the other hand, with six aldehydes—



In all cases condensation took place by the solution of the sodium carbide in an ethereal solution of the aldehyde. By this means ten acetylenic alcohols were isolated, all new compounds.

Iodine Phenols.—P. Brenans.—During the action of iodine on sodium phenate, the latter being in suspension in carbon disulphide, M. Schall obtained with orthoiodo-

phenol a triiodophenol and a diiodophenol, to which substances he gave no definite constitution. The author's present research establishes that the triiodophenol derivative is the compound $\text{OH}-\text{C}_6\text{H}_2-\text{I}_3$ (1, 2, 4, 6), and the diiodophenol derivative is $\text{OH}-\text{C}_6\text{H}_3-\text{I}_2$ (1, 2, 6).

Action of Crystallised Arsenic Acid on Pinene.—P. Genvresse.—During the action of arsenic acid on pinene the author obtained a body having a different odour from that of essence of terebenthine, a certain amount of terpinene, in addition to a little cymene and terpinol, being formed.

MISCELLANEOUS.

Dr. Morris Travers's Book on "The Study of Gases."—In our review of this book in the *CHEMICAL NEWS* for February 28th, we remarked on the absence of the plates of spectra of certain gases. We understand from Messrs. Macmillan, the publishers of the book, that the omission of these plates was due to an accidental oversight on the part of the binder, and was confined to a few only of the early copies which were sent to the Press for purposes of review. An examination of the plates confirms the opinion we expressed that they would be of the greatest value to all engaged in the study of the newly discovered inert gases of the atmosphere.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. It was announced that his Royal Highness the Prince of Wales had graciously consented to become Vice-Patron of the Institution. Sir William Agnew, Bart., Mr. Hilder Daw, Mr. J. F. W. Deacon, Mrs. Deacon, Mr. A. St. John Clerke, Miss Agnes M. Clerke, Mr. E. Figgess, Mr. M. Fitzmaurice, Mr. F. M. Guedalla, Dr. R. Harold, Mr. F. Legge, Dr. H. Lewkowitsch, Miss A. H. Little, Mr. W. F. Preedy, Dr. A. M. Robson, Mr. M. M. Samuel, Mr. F. A. Smith, Mr. J. J. Torre, Major-General James Waterhouse, Mr. Philip Watts, F.R.S., and Mr. C. Tweedale were elected Members. The special thanks of the Members were returned to "An Old Member" for a donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

The Iodisation of the Mixed Hydrocarbides.—A. Erdinger and P. Goldberg.—Following up their previous researches, the authors have endeavoured to utilise for the purpose of iodising certain substances the decomposition undergone by iodide of sulphur under the influence of certain reagents; as is well known iodide of sulphur is decomposed when heated with HNO_3 ($D=1.2$), and they have attempted to utilise this reaction. Their first object was to examine this reaction, in such cases where the known methods of ioduration are not applicable, or only give bad results; such is particularly the case with the mixed aromatic hydrocarbides. Among other results the authors have found that their method renders possible the direct introduction of iodine into the radical of the aromatic compounds without attacking the lateral chain, so that mono-iodides can be obtained. The method has also been applied to the preparation of iodobenzene, although this compound has already been obtained, with excellent returns, by Neumann and Istrati, by iodising in the presence of concentrated sulphuric acid. For iodobenzene, for example, they heat on the water-bath, with a vertical condenser, 10 grms. of benzene, 20 grms. of powdered iodide of sulphur, and 120 c.c. of HNO_3 ($D=1.34$) for two or three hours. The ortho- and para-iodotoluenes were prepared in an analogous manner, using benzene as the solvent; the ortho-iodoxylenes, mesitylene, durol, pentamethylbenzene, cymene, and naphthalene were submitted to the same process of ioduration, and as a rule good results were obtained.—*Berichte*, vol. xxxiii., p. 2875.

MEETINGS FOR THE WEEK.

- MONDAY, 10th.—Society of Arts, 8. (Cantor Lectures). "Photography applied to Illustration and Printing," by J. D. Geddes, F.R.P.S.
- Society of Chemical Industry, 8. "Birmingham Sewage and its Treatment," by F. R. O'Shaughnessy, A.R.C.Sc. (Lond.), A.I.C., &c. "Remarks on the Technical Examination of Glue," by E. G. Clayton, F.I.C., F.C.S.
- TUESDAY, 11th.—Royal Institution, 3. "Recent Researches on Protective Resemblance, Warning Colours, and Mimicry in Insects," by Prof. E. B. Poulton, M.A., Hon. LL.D., D.Sc., F.R.S.
- WEDNESDAY, 12th.—Society of Arts, 8. "The Utility of Alkaline Phosphatic Manures," by John Hughes, F.I.C.
- THURSDAY, 13th.—Royal Institution, 3. "Caricature in and out of Parliament," by E. T. Reed.
- Society of Arts, 4.30. "The Indian Famine of 1899, and the Measures taken to meet it," by Thomas William Holderness, C.S.I.
- FRIDAY, 14th.—Royal Institution, 9. "Magnetism in Transitu," by Prof. Silvanus P. Thompson, B.A., D.Sc., F.R.S.
- Physical, 5.
- SATURDAY, 15th.—Royal Institution, 3. "Some Electrical Developments," by Lord Rayleigh, F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. LXXXV., No. 2207.

THE ESTIMATION OF CARBON IN STEEL BY DIRECT COMBUSTION.

By RUDOLF L. LEFFLER, F.C.S.

MANY people entertain the opinion expressed in Arnold's "Steel Works Analysis" regarding the estimation of carbon in steel by direct combustion, viz., "the method may be dismissed as quite out of the running, so far as steel is concerned. It requires the material to be in a state of impalpable powder—a condition impossible to most steels."

There is some truth in this quotation if "direct" combustion is taken to mean the ignition in a stream of air or oxygen only, but there is little or no worth in it in relation to the direct combustion of steel with suitable oxidising reagents.

The direct combustion of steel in the dry way is not only a practicable procedure; it is an eminently desirable one, where correct results must be rapidly obtained and the sample is either in such a physical state or contains such elements as invalidate Eggertz's colour test.

The estimation is made as follows:—Throw the borings on to a sieve having 20 meshes to the lineal inch, which is fitted into another having 40 meshes to the lineal inch. From the portion which passes through the one and not through the other, weigh out 2.5 grms. and mix with 6 grms. of red-lead (the blank of which on 10 grms. should not exceed 0.010 gm.) by shaking in a small weighing bottle. Transfer the mixture to a porcelain boat ($4 \times \frac{3}{4}$), and place in the water-bath until ready for ignition.

The combustion is conveniently made in a porcelain tube ($20 \times 1\frac{1}{2}$), containing CuO for a few inches of its length and fitted at one end with means of purifying the incoming air or oxygen, and at the other end with a simple CaCl₂ drying tube. Lead chromate for absorbing sulphur compounds, or anhydrous CuSO₄ pumice for absorbing HCl, as in the ordinary combustion train, can be dispensed with, as the former never escape from the boat and the latter are not present. When the combustion-tube is at a red heat and the KHO bulb in its place, then insert the boat and quickly replace the stopper. There is no noteworthy evolution of gas due to a reaction between the sample and reagent such as takes place when ferrochromiums are suddenly heated in this way, and therefore, after having attached the aspirator and turned the taps full on, the combustion needs no further attention. With a good hot furnace combustion is complete in half-an-hour, even when air only ($2\frac{1}{2}$ litres) has been passed through. If the attached KHO bulb is so warm that it increases 4 or 5 milligrams, on standing in the balance case, it is best to work two bulbs alternately, but otherwise the bulb is re-weighed and replaced and a fresh combustion proceeded with. When drawn from the hot tube the contents of the boat are soft and can be easily scraped out with a suitably shaped piece of metal. The boat may then be used over and over again, but it should show no fine cracks or other signs of local weakness before being used, as it is then liable to break during ignition and mess the inside of the tube. Besides being otherwise objectionable, a coating of litharge increases the original tendency the tube has to crack on being suddenly heated.

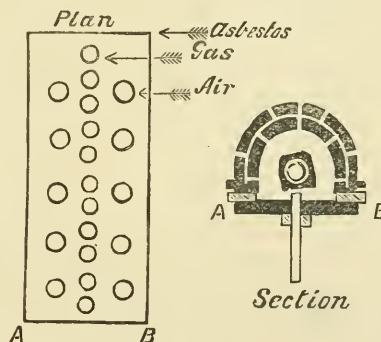
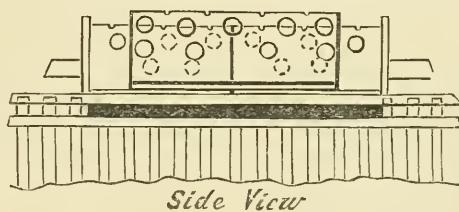
For direct combustion a hot furnace is necessary. I use one of the Bunsen type, in which the customary toothed fire-clay tiles are replaced by asbestos arches. These enable a very high temperature to be obtained from only a moderate gas supply; particulars of their construction are given by Jervis (Assistant in this Laboratory) in the CHEMICAL NEWS, vol. lxxvii., p. 5. The figure shows

a side view and section of the arrangement when a second larger cover is used to increase the heat over the portion of the tube occupied by the boat.

It may be asked if there is not some danger of the sievings from a sample containing more or less than its due proportion of carbon. I believe no source of error is to be feared with the medium sievings than attaches to the weighed amount taken in the ordinary way from the packet of coarse and fine. Special tests made on a series of standard steels showed that the carbon percentage with the coarse and fine portions were practically the same. The figures were:—

On coarse borings.	Through 30-mesh sieve.
0.136	0.120
0.457	0.457
0.758	0.754
1.060	1.036
1.243	1.243
2.286	2.291

Although sieving seems desirable, in order that material uniform in size and requiring about the same time to burn may be obtained, it must be said that any class of



borings made with ordinary care are completely decarbonised on heating with red-lead, but an extra fifteen minutes should be allowed in order to decompose any extra thick pieces. By still further increasing the period of ignition, chunks as large as peas and strips of sheet steel have been satisfactorily burned.

Below are given some results compared against those by dissolving in an acid solution of copper-ammonium chloride (5 per cent HCl), filtering, and ignition of the carbonaceous residue. (See Table, next column).

Direct combustion is particularly adapted to the estimation of carbon in special steels, such as tungsten and chromium-tungsten self-hards. As these borings are always thin, no sieving is ever necessary.

Attention has frequently been called to the fact that with ordinary carbon steels lower results are obtained with neutral solutions than with an acid solution of the double copper salt, and this is explained either by loss of hydrocarbons on dissolving or by the solubility of the residue in the menstruum. So far as steels containing special elements that are likely to exist as carbides are concerned, it seems equally important to point out that an acid solution of the double copper salt, as well as the acid (HCl) used subsequently for washing, may decompose or dis-

Acid solution of
double copper salt.

Per cent C.

0.15

0.19

0.23

0.27

0.49

0.58

0.70

0.93

1.27

1.39

1.45

1.55

1.87

Direct
combustion.

Per cent C.

0.15

0.19

0.25*

0.27

0.48

0.57

0.71

0.94

1.29

1.38

1.44

1.54

1.88

* Chunks as large as peas, specially picked out.

solve a portion of the metallic carbides. A friend using the direct combustion always finds this method to give the higher results, as much as 0.10 per cent.

The filtration of this class of steel, especially after forging, &c., on account of the fine state of division of the residue and its slimy nature, is somewhat troublesome, for as soon as the washings lose their acidity the residue comes through the filter. To overcome this difficulty, and at the same time the (probable) decomposing action of the hydrochloric wash, pure methylated spirit is used in this laboratory for washing, with extremely satisfactory results; although, on the average, the direct combustion gives the slightly higher—and probably more correct—figures.

Residue washed with
methylated spirit.

Per cent C.

0.42

0.63

0.86

1.06

1.20

1.25

1.34

1.42

1.64

1.88

2.08

2.50

Direct.

Per cent C.

0.45

0.65

0.89

1.10

1.22

1.27

1.38

1.44

1.66

1.90

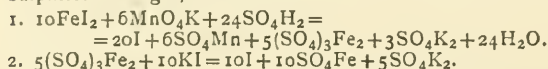
2.08

2.53

This direct estimation of carbon in steels was first tried in this laboratory in 1898. Since then at least two hundred of the results thus obtained have been checked by the ordinary process, and while, with the exception of special steels just named, the results have been in agreement, there were three or four samples of steels which were higher by the direct combustion without any assignable reason.

The Laboratory,
Messrs. Thomas Firth and Son, Lim.,
Sheffield.

Volumetric Estimation of Syrup of Iodide of Iron.—E. Rupp.—To effect this estimation, we add to 5 grms. of the syrup, diluted with water, acidulated with sulphuric acid, a solution of permanganate of potash at $\frac{1}{100}$ th until the colour is persistent; after about two or three hours, potassic iodide is added; it is again left for an hour, and the iodine then titrated with one-tenth normal hyposulphite. We get, in fact:—



These equations show that 10FeI₂ gives 30I; 1 c.c. of hyposulphite corresponds to 0.2066 per cent of FeI₂ in the syrup.—*Arch. de Pharm.*, vol. ccxxxviii., p. 159. [It would be interesting to know what precautions the author takes to prevent or to allow for the reduction of the permanganate by the sugar].

ON THE DETECTION OF SMALL QUANTITIES OF ARSENIC IN FOODS, ESPECIALLY IN BEER.

By J. C. BERNTROP, Chemist at the Chemical Laboratory of the
Municipal Sanitary Service of Amsterdam.

THE following simple method for detecting small quantities of arsenic in beer, &c., has been employed by me:—One litre of the beer is taken, a few drops of bromine added, and the mixture well shaken in order to convert the arsenious acid into arsenic acid. The liquid is allowed to stand for twenty-four hours, and then made strongly alkaline with ammonia. After adding 5 c.c. of a saturated solution of sodium phosphate, and 10 c.c. of the ordinary magnesia mixture, the liquid is allowed to stand for twenty-four hours in a moderately warm place. The precipitated ammonium-magnesium phosphate carries down with it the arsenic as ammonium-magnesium arsenate.

The clear liquid is poured off, and the precipitate transferred to a filter as completely as possible, then dissolved from the filter with 50–100 c.c. of warm dilute sulphuric acid (20 per cent).

The solution is run into the flask used for the precipitation, to dissolve the remainder of the crystalline precipitate adhering to the side of the flask.

The solution is heated in a Kjeldahl flask, small quantities of nitric acid being added from time to time until the liquid is totally decolorised and sulphuric acid begins to escape. This treatment is necessary in order to destroy the albumenoids which otherwise would occasion the development of hydrogen sulphide when using the Marsh or the Gutzeit test, for which the liquid is now ready.

The method has proved to be likewise useful in the examination of other drinks and of food.

With great interest all chemists will have read the "Report of the Joint Committee of the Society of Chemical Industry and of the Society of Public Analysts on the Detection and Approximate Estimation of Minute Quantities of Arsenic in Beer, Brewing Materials, Food-stuffs, and Fuels."

I think that as my method allows the use in one manipulation of one litre of beer—the committee experiments on ten or twenty c.c. of beer—it may be a useful addition to theirs.

Dionine.—This substance, prepared by E. Merck, of Darmstadt, is described as a mild and pleasant substitute for morphia and codeia; it is a derivation of morphia, having the composition expressed by the formula $\text{C}_{19}\text{H}_{23}\text{NO}_3\text{HCl} + \text{H}_2\text{O}$. It appears as a white, odourless, micro-crystalline powder of bitter taste, melting at 123–125°, and very easily soluble in water. The aqueous solutions possess a neutral reaction, and keep for a long time, clear and free from decomposition. Owing to its neutral character injections of dionine are not painful, whilst its greater solubility enables it to diffuse more readily into the circulation, and develop its action more quickly than any morphia derivative yet employed, it is also devoid of any toxic properties, and, according to the unanimous opinion of all observers, the taking of dionine never becomes a habit. According to experimental investigations by Hoff, intravenous injections of dionine cause immediate retardation of the respiration, and longer expirations and inspirations; under its influence the atmospheric air remains longer in contact with the capillary vessels of the lungs; the oxidation of the blood and the removal of the carbonic acid is therefore more complete, and the effect of the ventilation of the lungs increased.

Crystallisation of Peroxide of Iron.—Alfred Ditte.—It is known that when a mixture of hydrated iron sulphate and common salt is calcined, the oxide which results from the destruction of the crystalline ferrous salt in the middle of the fused salt can be separated out by repeated extraction of the fused mass with hot water. The author discusses the mechanism of this reaction.—*C. R.*, cxxiv., No. 9.

ON THE ANALYSIS OF PYRITIC RESIDUES.

By A. MINOZZI.

At the present time the sulphuric acid industry uses, almost entirely, sulphur from pyrites, a mineral composed essentially of bisulphide of iron. Pure pyrites contains 53.3 per cent of sulphur and 46.7 per cent of iron, but the natural product is rarely pure. It always contains gangue, copper, zinc, lead, arsenic, selenium, antimony, peroxide and protoxide of iron, and sometimes manganese, titanium, &c. Finally, phosphorus is often met with. The operation of roasting for the production of sulphurous anhydride leaves a residue (called *Purpurerz* or *Kiesabbrände* in Germany, and *purple ore* in England), in which the iron exists almost entirely in the form of the sesquioxide.

If the pyrites contains reasonable proportions of zinc or copper the residue is utilised for the extraction of these metals; if this is not the case, it forms, at all events for the Italian manufacturer, a most embarrassing by-product, on account of the large cost of transport. The idea of utilising these residues is by no means new. Metallic iron is present to the extent of 56 to 65 per cent, and as they only, as a rule, contain a small amount of phosphorus (less than 10 grms. per 100 kilogrms.) these residues form an excellent iron ore, and even yield a pig-iron of good quality.

I have recently had occasion to analyse various samples of pyritic residues with the idea of using them as iron ores. One sample contained 0.92 per cent of copper, another 0.85 per cent of titanium, and all contained 6.32–8.47 per cent of silica, 0.85–2.16 per cent of sulphur, 0.16–0.37 per cent of lead, and 0.005–0.021 per cent of phosphorus.

The proportion of iron varied from 57.12 to 60.81 per cent. With the exception of one only, which only contained traces, all the samples examined were free from arsenic. The estimation of the alkaline earthy metals was not made.

Every analyst knows how difficult it is to dissolve pyritic residues. Lunge recommends, for estimating the sulphur by his method, pulverising the material in an agate mortar. Borntraeger (*Zeit. Anal. Chem.*, xxxviii., 774) having observed that aqua regia does not dissolve calcined ferric oxide easily, but that this body is easily dissolved by hydrochloric acid containing free chlorine, iodine, or bromine, or peroxide of hydrogen or nascent hydrogen, advises the addition of peroxide of manganese free from iron to the hydrochloric acid. Under these conditions the chlorine which is evolved rapidly dissolves the ferric oxide. I have attempted to dissolve pyritic residues in hydrochloric acid containing chlorate of potassium, but even after twenty-four hours I have never obtained complete solution. It follows from the above that the ordinary wet methods of analysis must be abandoned if we wish for satisfactory results, and I hope that the methods I am about to describe for obtaining exact results as rapidly as possible will prove to be of use.

Sulphur.—For the estimation of sulphur I follow a modification of the fusion method described by J. Deutecom (*Ibid.*, xix., 313) and applied by the author to pyrites. I had, in fact, observed that this method is superior to and more rapid than fusion with a mixture of carbonate of soda and nitrate of potassium. Two grms. of the pyritic residue are weighed out accurately in a platinum crucible, and intimately mixed with 5 grms. of a mixture composed of 2 parts of anhydrous carbonate of sodium and 1 part of chlorate of potassium; the whole is then covered with 2 grms. of the same mixture. Although coal-gas of good quality is almost free from sulphuretted hydrogen, it is not safe to heat the crucible on a triangle; I prefer a sheet of asbestos card with a circular hole in the middle, which will just hold the covered crucible. By this arrangement the products of combustion from the source of heat do not come into contact with the fused mass, and therefore cannot falsify the results. We begin by heating gently

until the top layer of pure mixture is fused; this should take about half-an-hour. The heat is then gradually increased, and after another ten minutes the gas is turned full on; the mass, from being pasty, becomes solid, then reverts to a semi-fluid condition, and then becomes pasty again. Care must be taken to reach this point so as to be certain of the complete decomposition of the perchlorate. After cooling, the crucible with its contents and the cover are thrown into a beaker containing about 300 c.c. of warm water, and allowed to digest, warm, until the whole of the melted mass is disaggregated. The clear liquid is then decanted through a small filter and collected in an Erlenmeyer matras with a flat bottom, of about 1 litre capacity. The residue is washed by decantation, five or six times, with a 2 per cent solution of dry carbonate of sodium, using about 50 c.c. of the solution for each washing; it is then finally heated to boiling. The last wash-waters should no longer give any sulphuric acid reaction, and only traces of hydrochloric. The wash-waters added to the principal liquor make about 600 c.c. Forty c.c. of 10 per cent hydrochloric acid are added, and the whole heated to boiling to completely remove all the carbonic acid, and the sulphuric acid is precipitated by 10 c.c. of 10 per cent chloride of barium, taking the usual precautions.

Silica, Lead, Titanium, Copper, and Iron.—Five grms. of the pyritic residues are placed in a platinum crucible of about 30 c.c. capacity, and while heating gently about 25 grms. of bisulphate of potassium are gradually added. The temperature is gradually raised until the melted mass is homogeneous. After cooling, it is treated with 500 c.c. of 2 per cent sulphuric acid and filtered, the filtrate being collected in a graduated litre flask. The residue is washed with boiling water, slightly acidulated with sulphuric acid, then dried, calcined, and weighed. It is then moistened with 5 c.c. of 10 per cent sulphuric acid and 20 per cent hydrofluoric acid, and carefully evaporated. The last traces of sulphuric acid are neutralised by the addition of a small quantity of carbonate of ammonium, after which it is calcined strongly until the weight remains constant. The difference between the two weights represents the amount of silica present in the original sample.

The residue, which still contains a little ferric oxide, is again fused with bisulphate of potassium, dissolved in sulphuric acid, and added to the principal solution, which is then made up to a litre. The insoluble part consists mainly of sulphate of lead; it is treated several times with a concentrated boiling solution of acetate or tartrate of ammonium; the lead is precipitated by sulphuretted hydrogen, and estimated in the form of sulphate after having been re-dissolved in nitric acid.

As for the principal solution, 100 c.c. are taken for the estimation of the iron, and the remainder, which serves for the estimation of the other elements, is evaporated down to about 300 c.c. To estimate the titanium in iron ores, Brakes (*Journ. Soc. Chem. Ind.*, xviii., 1097) reduces the hydrochloric solution of the ore with a solution of sulphurous acid; Baskerville (*Monteur Scientifique*, Oct., 1900, p. 697) treats the hydrochloric solution with a current of gaseous sulphurous anhydride, but I prefer a solution of sodium bisulphite, prepared by means of a 50 per cent solution of crystallised carbonate of soda. In this manner I obtain a solution containing 21 per cent of available sulphurous anhydride.

The concentrated portion of the principal liquor is placed in an Erlenmeyer matras of about 600 c.c. capacity, and neutralised with ammonia; it is then made slightly acid with hydrochloric acid, and treated with bisulphite of sodium; the titanous and phosphoric acids are precipitated in a slightly coloured flocculent form. This precipitate is collected on a filter, washed with boiling water, and then fused with about 2 grms. of a mixture composed of 2 parts of carbonate of sodium and 1 part of nitrate of potassium. The melted mass is taken up with 200 c.c. of boiling water, the phosphate of sodium formed is dis-

solved, while the residue of titanate of sodium and ferric oxide is collected on a filter. This is fused with bisulphate of potassium, and the treatment with bisulphite of sodium is repeated; in this manner perfectly pure, white titanate acid is obtained, which is calcined and weighed. As for the phosphoric acid remaining in solution, it is precipitated in the form of phospho-molybdate of ammonium, and estimated in the form of pyrophosphate of magnesium.

The solution, thus freed from titanium and phosphorus, is treated with a little bisulphite of sodium, acidulated with 50 c.c. of 10 per cent hydrochloric acid, and submitted while warm to the action of a current of sulphuretted hydrogen.

The precipitated sulphides, after washing with sulphuretted hydrogen water, are calcined in a small porcelain crucible, and the residue is dissolved in nitric acid. The solution obtained is made alkaline by ammonia, then treated with a small quantity of carbonate of ammonium, and heated on the water-bath for some hours.

It is then filtered, and the copper is estimated in the filtrate either by the electrolytic method, or gravimetrically, by precipitating and weighing it in the form of cuprous sulphide.

In 100 c.c. of the principal sulphuric solution the iron is estimated by permanganate, either directly or after separation in the state of basic carbonate if the pyritic residues contain manganese, zinc, and other metals.—*La Chimica Industriale*, vol. ii., p. 248.

ESTIMATION OF THE PHOSPHORIC ACID IN PHOSPHATES.

By J. A. MULLER.

THE estimation of the titration value of the uranium solution serving for the volumetric estimation of the phosphoric acid in phosphates is often done by means of a titrated solution of crystallised phosphate of sodium. The facility with which this salt loses moisture does not, however, admit of any great accuracy. The crystallised salt of phosphorus, $\text{PO}_4\text{HNaNH}_4\cdot 4\text{H}_2\text{O}$, is much more stable in this respect. This salt, pulverised and spread in a thin layer in a crucible, only loses 0.15 per cent of its own weight in the space of four hours at 18° in the air, of which the hygro-metric degree was equal to 0.5, while, under the same conditions, the crystallised phosphate of sodium loses 2.40 per cent. Even when placed over phosphoric anhydride, this crystallised salt of phosphorus only undergoes a slight loss of weight, 1.68 per cent after twenty-four hours at the ordinary temperature, while crystallised phosphate of soda ends, in this case, by becoming almost, if not quite, dehydrated.

However, this salt of phosphoric is far from possessing the stability of crystallised dicalcic phosphate, $(\text{PO}_4)_2\text{Ca}_2\text{H}_2\cdot 4\text{H}_2\text{O}$, which, when freely exposed to the air and under the preceding conditions, or even over phosphoric anhydride, does not vary in weight at all at the ordinary temperature. We can also recommend a nitric solution of this phosphate—in which the proportion of phosphoric acid has previously been determined—to determine the value of the uranium solution serving for the titration of commercial phosphates.

To prepare the crystallised dicalcic phosphate, we gradually add a cold dilute solution of disodic phosphate to a dilute solution of pure chloride of calcium until the almost complete precipitation of this metal is effected. The precipitate, which is gelatinous at the moment of its formation, rapidly becomes crystalline; it is easy to wash it completely. When washed, it is thrown on flat plates and dried in the oven at a temperature of about 70° . Theoretically, the salt thus obtained should contain 41.27 per cent of P_2O_5 . The estimation of this substance in the state of magnesian pyrophosphate, after precipitation

in the form of phosphomolybdate and ammonio-magnesian phosphate, gave 41.45 and 41.38 per cent of P_2O_5 . By estimating the phosphoric acid by means of citro-magnesian solution, I found 41.55 and 41.29 per cent.

With regard to this latter method of estimation, an important remark may be made. The first precipitate of ammonio-magnesian phosphate—obtained by adding the citro-magnesian solution, then an excess of ammonia to the nitric solution of the phosphate—contains a small quantity of calcium. To separate this, the precipitate is re-dissolved—after separation from its mother-liquor—in nitric acid, a small quantity of citro-magnesian solution, chlorhydrate of ammonium, and then ammonia are added; after twelve hours, it is filtered, and the precipitate washed with ammoniacal water, &c. It is advisable to conduct this last operation in a platinum crucible, which will serve to calcine the ammonio-magnesian phosphate.

It may also be remarked that the precipitate obtained by adding the magnesian mixture to an ammoniacal solution of phosphomolybdate contains, or may contain, a little molybdenum, which can be separated by re-dissolving the precipitate in hydrochloric acid and re-precipitating by ammonia in the presence of a little of the magnesian mixture.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 23.

THE ATOMIC WEIGHT OF ANTIMONY.*

By G. CLAUSEN FRIEND and EDGAR F. SMITH.

KNOWING that antimony oxide could be completely expelled from its combinations in a current of hydrochloric acid gas, it appeared probable that a new ratio might be established for antimony, by exposing potassium antimonyl tartrate to the action of this gas. It will be recalled that by this procedure the atomic weights of molybdenum and arsenic had been previously determined in this laboratory. In these particular instances sodium molybdate and sodium pyroarsenate were exposed in porcelain boats, at a moderate heat, to the action of the gas, and from the weight of the residual sodium chloride the respective atomic weights were calculated. The method of work adopted with these metals was pursued with potassium antimonyl tartrate, but it was soon discovered that as carbon dioxide and water escaped the salt swelled up and was projected from the boat, so that a double crucible was substituted for the latter. On trial this device proved to be perfectly satisfactory, and it was possible in a crucible No. 00, from 1 to $1\frac{1}{4}$ inches in height, to operate with as much as 3 grms. of material. The appended sketch represents the apparatus in detail.

A steady stream of hydrochloric acid gas was generated in the large flask by acting with pure, concentrated, sulphuric acid upon hydrochloric acid of like character. The gas was sufficiently dried by its passage through sulphuric acid and a column of calcium chloride, and then introduced through a porcelain delivery tube into the crucible. The smaller crucible was supported in the larger one upon a perforated porcelain plate. The lid of the larger crucible had two openings, one for the entrance, and the other (A) for the exit of the excess of acid gas. Platinum crucibles should not be used; they are very severely attacked by the acid vapours.

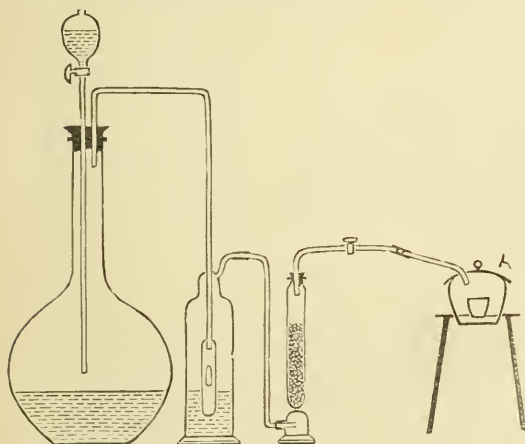
In the experiments the dry gas was passed over the salt in the smaller crucible for half-an-hour, before any heat was applied. At the expiration of this period a small flame was placed under the crucible, and it was heated to 150° for two hours, after which the temperature was gradually increased until the outer crucible showed a dull red colour. This temperature was maintained until all of the volatile matter was expelled, when a stream of oxygen was substituted, for half-an-hour, for the acid. Most of the carbonaceous material was removed in this

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xxxiii., No. 7.

way, when the acid vapour was again introduced, and the crucible contents allowed to cool in it. As the residual potassium chloride contained some carbon, it was dissolved in water, and the solution filtered. The filtrate, with washings, was collected in a weighed platinum dish and evaporated upon a water-bath. The dish was supported upon a perforated glass plate. The dry potassium chloride was finally heated in an air-bath to 150°, then removed and gently heated over a flame to expel the last traces of moisture. On cooling, the salt was weighed. Two experiments made with potassium antimonyl tartrate, not especially purified, and with an ordinary balance and weights, gave the following results:—

	Salt. Grms.	Potassium chloride. Grm.	Atomic weight of antimony.
1	2.0358	0.4691	120.44
2	2.5919	0.5973	120.41

This concordance in result and the ease with which the method could be executed, led us to prepare and purify large quantities of potassium antimonyl tartrate. To this end the purest commercial salt was re-crystallised ten times, the first fraction only being used in each subsequent



crystallisation. The final 50 grms., intended for experiment, were dried at 150° for a period of sixteen hours. A weight was taken, and the mass then again heated, cooled, and re-weighed. There was no variation in the weight. This material was carefully tested for impurities (e.g., arsenic, sodium, silica, &c.), and was found free from them. Portions of it were then acted upon as outlined in the preceding paragraphs.

TABLE A.

	Potassium antimonyl tartrate. Grms.	Potassium chloride. Grm.	Atomic weight of antimony.
1 ..	1.19481	0.27539	120.345
2 ..	1.57004	0.36186	120.359
3 ..	2.00912	0.46307	120.351
4 ..	2.04253	0.47073	120.379
5 ..	2.16646	0.49935	120.341
6 ..	2.25558	0.51982	120.385
7 ..	2.61255	0.60215	120.350
8 ..	2.95272	0.68064	120.311

Mean = 120.353

Maximum = 120.385

Minimum = 120.311

Difference 0.074

The balance used in the subsequent experiments was constructed for atomic weight work by Troemner. It

is sensitive to $\frac{1}{10}$ of a milligram. with or without load. The weights of brass and platinum were carefully calibrated. All weighings were reduced to the vacuum standard. The specific gravity of potassium chloride was taken as 1.995 and that of the tartar emetic as 2.6 (Beilstein). The atomic weights used in the calculations were O=16, H=1.008, C=12, K=39.11, and Cl=35.45. The results obtained with the pure material and with the observance of all the necessary precautions are shown in Table A.

The barium and silver antimonyl tartrates crystallise well, and the hope was entertained that these salts might also be included in the circle of experimentation, but thus far the results with them have not been satisfactory.

ON PYRITE AND MARCASITE.*

By H. N. STOKES.

(Continued from p. 115).

X. MISCELLANEOUS SPECIMENS AND SPECIMENS OF DOUBTFUL NATURE.

WITH the aid of the pyrite-marcasite curve we are now in a position to determine the quantitative composition of specimens of pyrite and marcasite in regard to which there is some uncertainty. The supposed nature of the specimens, according to the geologist, mineralogist, or dealer from whom they were obtained, is stated, as well as the composition established by my method. It is to be understood that the figures express the relative amount of pyrite and marcasite on a scale of 100, impurities being excluded. In this connection I wish to acknowledge the generosity of Dr. A. A. Julien, who has placed at my disposal a number of the identical specimens described by him in his valuable paper repeatedly referred to above. As the study of these specimens is especially important in confirming or refuting his hypothesis (see Section VI.), I have grouped them together at the end of this section, and have in each case quoted his original description and specific gravity determination, comparing in parallel columns the results obtained by the specific gravity and the oxidation methods.

Notes to Table A.

- No. 15. Nearly spherical concretion from coal; locality unknown. Weight, 9.2 grms. Very hard. The structure is coarsely fibrous and radial, with concentric shells of pyrite and marcasite, easily distinguishable by their colour.
- No. 16. Pyritised ammonite from Folkestone, England. The walls of the cavities are encrusted with pyrite crystals, but the nature of the mass cannot be determined from the colour.
- No. 17. Concretion from Red Cloud Mine, San Juan County, Colorado, supposed to be marcasite. It consists of a finely fibrous incrustation on rhyolite, varying in thickness from 1 to 10 m.m., with mammillary surface, and with a banded structure and cleavage perpendicular to the fibres. The banded structure is due to the enclosure of quartz and a black substance which, judging from the presence of a little copper, lead, and arsenic, may be galena, arsenopyrite, and chalcocite. The latter would account for the high oxidation coefficient, which could not be caused by the first two (see p. 92). Carefully selected material gave a specific gravity of 4.563.
- No. 18. The occurrence of this material is thus described by Mr. Lindgren, by whom it was submitted for a determination of the yellowish grey material:—
"This specimen is derived from the Present Need Mine, Quartzburg district, Grant County,

* From the Bulletin of the U.S. Geological Survey, No. 156.

TABLE A.—Quantitative Composition of Specimens of Doubtful Nature.
(Figures in parenthesis were determined by the indirect method).

No.	Original designation, &c.	Locality.	p .	Pyrite. Per cent.	Marcasite. Per cent.
15.	Concretion from coal	Unknown	30.1	63.0	37.0
16.	Pyritised ammonite.. ..	Folkestone, England	46.9	88.0	12.0
17.	Fibrous marcasite	Red Cloud Mine, Colorado	65.7	100.0	—
18.	Pyrite with marcasite	Quartzburg district, Oregon	38.6	78.0	22.0
19.	Marcasite	Chautauqua Tunnel, Idaho.. ..	51.3	93.5	6.5
20.	Marcasite	Garfield Tunnel, Idaho	19.8	30.5 (34.4)	69.5 (65.6)
21.	Marcasite nodules	South Dakota.. ..	60.3	100.0	—
22.	Marcasite (selected).. ..	Littmitz, Bohemia	19.5	29.5 (27.8)	70.5 (72.2)
23.	Marcasite (selected).. ..	Crow Branch Mine, Wisconsin	18.6	26.0 (31.0)	74.0 (79.0)
24.	Fibrous marcasite	Sunshine, Colo.	52.2	(a) 94.0	(b) 6.0
25.	Marcasite after pyrite	Folkestone, England	55.4	97.0	3.0
26.	Pyrite ore	Rio Tinto, Spain	65.7	100.0	—
27.	Pyrite octahedra	Unknown	80.4	100.0	(c)
(a) Or more.		(b) Or less.		(c) Much cobalt.	

TABLE B.—Quantitative Composition of Julien's Specimens.
(The numbers in parentheses are those given in Julien's paper).

Number.	Locality.	Density.	p .	Composition deduced from p .	Composition according to Julien, deduced from density.
28. (Pyrite 1)	Galena, Ill.	5.015	60.3	Pyrite.. .. 100.0	Much Marcasite.
29. (Pyrite 96)	Franklin, N.J.	4.856	59.0	Pyrite.. .. 99.5	{ Pyrite.. .. 27.51 Marcasite .. 72.49
30. (Pyrite 98)	Somerville, Mass.	4.843	59.6	Pyrite.. .. 99.5	{ Pyrite.. .. 21.18 Marcasite .. 78.82
31. (Pyrite 101)	Monroe, Conn.	4.819	60.7	Pyrite.. .. 100.0	{ Pyrite.. .. 9.38 Marcasite .. 90.62
32. (Pyrite 106)	Bastrop, Texas	4.791	67.7	Pyrite.. .. (a) 100.0	{ Pyrite.. .. 1.00 Marcasite .. 99.00
33. (Marcasite 1)	Cumberland, England.	4.987	42.9	{ Pyrite.. .. 83.0 Marcasite .. 17.0	{ Pyrite.. .. 89.45 Marcasite .. 10.55

(a) Contains nickel.

Oregon. The vein, carrying chiefly gold, partly in free form, partly associated with sulphides, is contained in diabase and diabase-porphry. The ore minerals are normal yellow pyrite, a soft yellowish grey material supposed to be marcasite, zinc blende, and chalcopyrite." The iron sulphides are easily separated from the rock and other sulphides by hydrofluoric acid. The yellowish grey material, which is closely veined with pyrite, could not be separated from the latter, but the oxidation coefficient of the mixture indicates that it is marcasite. The portion examined contains a trace of copper and lead and no zinc.

No. 19. This is thus described by Mr. Lindgren:—"This specimen is taken from the dump of the Chautauqua Tunnel, at De Lamar, Owyhee County, Idaho. The specimen consists of quartz, upon which there is a crust of pyrite. The quartz itself contains arborescent forms of a mineral supposed to be marcasite, and described as such in *Twentieth Annual Report, U.S. Geological Survey, Part III.*, p. 130." The mineral in question was easily separated from the quartz and the mass of the pyrite by digestion with hydrofluoric acid. It formed dark coloured tabular masses, presenting no definite crystalline form, and containing traces of copper and lead with a notable amount of arsenic. The oxidation coefficient (51.3) shows that it consists of at least 93.5 per cent of pyrite, but the proportion thus determined is somewhat too low, owing to the influence of the arsenic.

No. 20. Thus described by Mr. Lindgren:—"This specimen is taken from the Garfield Tunnel, 250 feet from the portal, near De Lamar, Owyhee County, Idaho, and is described in *Twentieth Annual Report, U.S. Geological Survey, Part III.*,

pp. 131 and 171. The specimen consists of a soft white material, which, according to analysis, is probably kaolinite mixed with sericite. It contains arborescent forms of marcasite." The supposed marcasite was isolated by hydrofluoric acid. It could not be definitely described as such from the colour and crystalline form. As the oxidation coefficient (19.8) was too high for pure marcasite, a portion was mixed with one-ninth its weight of pyrite, and then gave—

$$p = 22.6 = 41 \text{ per cent pyrite.}$$

We have, then—

$$0.9x + 10 = 41, \text{ or } x = 34.4.$$

This corresponds to $p = 20.6$, a number agreeing within permissible limits with the original determination. We have, therefore,—

Pyrite directly determined .. 30.5 per cent

Pyrite indirectly determined. 34.4 "

and the original conclusion of Mr. Lindgren is only in part confirmed. A little arsenic is also present.

No. 21. Material supposed to be marcasite, from South Dakota. Submitted by Dr. G. P. Merrill. The sample consists of spherules not over $\frac{1}{2}$ m.m. in diameter, and so brittle as easily to be crushed by the finger. They had undergone vitrification to such an extent that the original substance was entirely concealed in the mass of sulphate. The oxidation coefficient shows that the material is pyrite, and the analysis that some copper is present. The normal value of p indicates that the copper is probably in the form of chalcopyrite.

No. 22. Marcasite from Littmitz, Bohemia, consisting of flat deeply striated twins of marcasite on a nucleus which on fracture shows both marcasite and pyrite. Only the portions free from visible ad-

mixture of pyrite were taken for examination, and gave $p=19.5$. Admixture with one-ninth pyrite gave $p=21.0=35$ per cent pyrite. We have, then,—

Pyrite directly determined .. 29.5 per cent
Pyrite indirectly determined . 27.8 „

(Regarding the Littmitz marcasite, see Sadebeck, *Monatsber. K. Preuss. Akad. Wiss. Berlin*, 1878, vol. xx., p. 19; and Hintze, "Handbuch der Mineralogie," vol. i., pp. 732, 825).

- No. 23. A specimen from Crow Branch Mine, Wisconsin, consisting of a compact nucleus of tin-white marcasite covered with crystals which are completely enclosed in elongated tubes of pyrite, the line of demarcation being clearly discernible on the fracture by the difference of colour. Selected portions free from visible admixture of pyrite were used, giving a specific gravity of 4.89. To determine the contents of pyrite the indirect method was used.

Pyrite directly determined .. 26.0 per cent
Pyrite indirectly determined . 31.0 „

As only the powdered material was available for the indirect determination, the difference is not surprising (see p. 82).

- No. 24. Material from Sunshine, Colorado. Finely fibrous radial concretions in quartz, which on the freshly cleaned fracture show a faint banded structure. Supposed to be marcasite. A little lead and copper and much arsenic and antimony are present. As arsenic, and probably antimony, would lower the oxidation coefficient, the figure given for pyrite is too low, and the presence of marcasite is doubtful.
- No. 25. A large flattened concretion from Folkestone, England, described as "marcasite after pyrite." The fracture is columnar and the surface is covered with rounded projections, apparently tetragonal pyramids, possibly of the type described by Penfield (*Am. Journ. Science*, 1889, Series 3, vol. xxxvii., p. 209). The colour on the freshly-broken surface exactly matches pyrite. I have received several other supposed marcasite concretions from Folkestone, all of which are clearly pyrite.
- No. 26. Pyrite ore from Rio Tinto, Spain. The fragments are greyish, evolve some hydrogen sulphide with acids, and with the bromine hydrogen sulphide test (p. 115) show very finely disseminated copper sulphide.
- No. 27. Brilliant untarnished octahedra in calcite, containing a large amount of cobalt and a little copper, which explains the abnormal oxidation coefficient.

Conclusions.

Of the above thirteen specimens five have been described as marcasite, though consisting nearly or entirely of pyrite, while three other marcasites are shown to contain a large amount of pyrite, which could not be detected without the aid of the oxidation method. As these samples were selected and examined without preconception as to their nature, it seems probable that a very considerable proportion of the concretions which exist in collections or are sold as marcasite are in reality pyrite, while not a few others, even when fairly well characterised by rhombic crystallisation, may contain inclosures of pyrite.

Dr. Julien's Specimens.

The following descriptions are in part quoted from Julien's paper:—

Notes to Table B.

- No. 28. "Concretionary nodule. Marsden's diggings, Galena, Ill. No. 1 (fibrous core). Marcasitic pyrite. Very finely fibrous, pale brass-yellow

and splendid." Analysis (Julien), SiO_2 , 0.110; Pb, 0.188; As, 0.056. The fracture varies from fibrous to prismatic, the prisms being evidently elongated cubes, with terminations consisting of cube modified by pyritohedron and octahedron.

- No. 29. "No. 96. Marcasitic pyrite. Franklin, N.J. Sharp, brilliant, brass-yellow, striated pyritohedra, yellowish-white, and splendid on fracture." No admixture of marcasite crystals. The value of p shows that they are practically pure pyrite, the low density being probably due to inclosures.
- No. 30. "No. 98. Marcasitic pyrite. Somerville, Mass. Very sharply defined, glittering yellowish cubes, sometimes distorted or rectangular, rarely striated, occasionally with octahedral planes upon their solid angles, yellowish white, and brilliant on fracture; scattered through a grey argillaceous slate."
- No. 31. "No. 101. Pyrite. Monroe, Conn. Deeply striated, distorted, brilliant cubes of very pale brass-yellow colour, with modifications by the pyritohedron; yellowish white, finely granular, and splendid on fracture, and sometimes inclosing grains of white quartz."
- No. 32. "No. 106. Marcasitic pyrite. Bastrop, Bastrop County, Tex. Dull and pale brass-yellow octahedra, rarely bright, very pale yellowish white, and brilliant on fracture; upon black granular crystalline hematite." The specimen contains a trace of arsenic, a strong trace of copper, and some nickel. It is the latter, possibly in conjunction with the copper, which causes the high oxidation coefficient.
- No. 33. "No. 1. Marcasite. Cumberland, England. Hollow incrustation pseudomorphs after barite, implanted on a group of barite crystals. The crusts are greyish white to tin-white, and splendid on fracture, with surfaces drusy with pseudo-octahedrons or rhombic pyramids, whose smooth, rectangular terminal faces (the basal pinacoid OP) project but slightly; a few minute rhombic prisms also occur, and some hexagonal though apparently triangular twins." The supposed rhombic pyramids with basis are evidently combinations of cube and octahedron belonging to the 83 per cent of pyrite which it contains.

Discussion of Julien's Hypothesis.

The above list includes some of the most pronounced cases of "marcasitic pyrite" described by Julien—that is, material with the crystalline form of pyrite, but supposed to consist very largely of marcasite. The four specimens, Nos. 29, 30, 31, and 32, consist of characteristic pyrite crystals, and if the oxidation method be admissible they are, in fact, free from marcasite, yet they all show abnormally low densities. The only conclusion which can be drawn from this is that the density alone does not afford a reliable means of detecting the presence of marcasite in pyrite unless the absence of all other contaminating substances be first conclusively proved, and that isometric crystallisation in itself affords a proof, almost amounting to certainty, that the sulphide is actually pyrite. It is undoubtedly true that perfect pyrite crystals may enclose marcasite, a good case of which is the Crow Branch specimen, No. 23, but such cases are comparatively rare, and the inclosure can usually be detected by breaking the specimen, and carefully examining the colour. In case of doubt a determination of the density is practically of no value, and resort must be had to the oxidation method. I have examined some of the marcasite specimens from the same collection, as well as others which are supposed to contain pyrite, and in general the latter can be detected by its colour after careful cleaning with acid. I have shown that certain specimens of marcasite do contain pyrite enclosed in such small masses as not to be capable of detection in this way

(Nos. 22 and 23). Small, warty excrescences on marcasite crystals are frequently pyrite, and when the conditions controlling the formation of the two sulphides are practically in equilibrium, these are likely not only to form but to be completely overgrown and enclosed in the crystal of marcasite. A marcasite which occurs mixed with visible masses of pyrite is therefore likely also to contain such inclosures which cannot be seen and whose presence can be detected only by the indirect oxidation method. That both pyrite and marcasite with abnormal density are essentially prone to decomposition is doubtless true, and while in certain cases this may be traced to an admixture of the two, in others it is due to inclosures of another nature. The lack of homogeneity not only permits the existence of fissures admitting air and moisture, but the formation of these is in such cases promoted by unequal expansion and contraction.

Fibrous marcasite is so often referred to that it may well exist, but so far as my somewhat limited range of examinations goes, a fibrous structure affords absolutely no presumption in favour of a specimen being marcasite; on the contrary, fibrous pyrite appears to be much more common than fibrous marcasite, the latter in concretions tending rather to assume the coarsely columnar structure.

XI. PARAMORPHISM.

The literature of the paramorphism of pyrite and marcasite is exceedingly scanty, and such as there is lends no support to the view that true transformation paramorphs exist. Those described are apparently either replacement or incrustation pseudomorphs, the true nature of which is shown by careful inspection. Wöhler (*Liebig's Annalen*, vol. xc., 256) attempted, without success, to convert marcasite into pyrite and pyrite into marcasite by heating for four hours at about 400°—experiments which are well worth repeating with an extension of the time and with the aid of the oxidation method. Julien's assumption of extensive paramorphism is scarcely longer tenable in view of the results described above, although the enclosure of considerable portions of pyrite in some specimens of marcasite lends some support to it. While theoretically possible, the attractive hypothesis that marcasite gradually changes to pyrite without re-solution, and that the porosity of certain pyrites can be thus explained, is thus far without a sound basis, either of experiment or of observation. It is intended to carry out experiments on this point in the immediate future.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 19th, 1902.

Prof. J. EMERSON REYNOLDS, Sc.D., V.P.R.S., President,
in the Chair.

MESSRS. E. A. Lewis, R. A. Berry, H. W. Crowther, and H. O. Jones were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Cyril Berghell, Checkley, Red Hill, Surrey; Ernest Boardman, 47, Knowsley Road, Smithills, Bolton; Charles Benson Davis, 218, West 134th Street, New York, U.S.A.; Arthur Hopwood, 49, Stanley Street, Tunstall; Jonathan Hugh Roberts, Oban Gwys, Swansea; Stephen Herbert Trimen, 61, St. John's Park, N.; William Wright Tunnicliffe, Newhall, Burton-on-Trent; William Charles Wain, Mercantile Explosive Dept., Sydney, N.S.W.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As Vice-Presidents—Prof. Meldola, F.R.S., and Prof. Frankland, F.R.S., *vice* Mr. Groves, F.R.S., and Prof. Purdie, F.R.S.

As Foreign Secretary—Prof. W. Ramsay, F.R.S., *vice* Prof. Meldola, F.R.S.

As Ordinary Members of Council—Mr. J. E. Marsh, Dr. J. A. Voelcker, Dr. A. Harden, and Dr. Lewkowsch, *vice* Mr. Fenton, F.R.S., Mr. Howard, Mr. Pope, and Dr. Crossley.

Mr. A. C. Chapman, Dr. Hewitt, and Dr. Thorne were appointed to audit the Society's accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Keith Benham Benham; Walter Geoffrey Black; Harry Burrows, Ph.D.; T. K. Buxy, M.A.; Frederick E. Catchpole, B.Sc.; Matthew Bradbury Challen; Kenneth Macomb Chance, B.A.; William Clifford; James Ward Daniels; Frederick Davis, B.Sc.; Evelyn Andros De la Rue, B.A.; William Dennis; John Kemp Smith Dixon; Charles Dorée, M.A.; Lewis Eynon; Alfred Vincent Elsdon; Eugène Arthur Fasnacht; Frederick Ferrand; John Oliver Ferrier; Clarence J. Green, B.Sc.; Paul Haas, B.Sc., Ph.D.; Noël Heaton, B.Sc.; Eugene Edwin Hennessey, B.A., B.Sc.; George Frederick Holdcroft; W. Holdsworth Hurlt, D.Sc.; William Brannan Jackson; David S. Smith Jardin; Selwyn Philip James Lavelle; Harry Lucas; Ernest Bowman Ludlam, B.Sc.; John Ross Mackenzie; William Maitland, B.Sc.; Francis Martin; Francis Hylton Molesworth; Alfred Holley Munday; Allan Ogilvie; Sydney Glyde Stephen Panisset; William Charles Ross; Nevil Vincent Sidgwick, M.A., D.Sc.; Frank Sturdy Sinnatt; Robert Eley Blake Smith, B.Sc.; William Southworth; Francis Bernard Stead, B.A.; James Swain; Lyon Vickers Turner; Arthur James Webb, B.A.; Charles Edward Womersley.

Of the following papers, those marked * were read:—

*24. "*The Union of Hydrogen and Oxygen.*" By H. B. BAKER.

Experiments have been made during the last ten years by H. B. Dixon, Victor Meyer, and by the author, with the object of seeing if the presence of moisture had any influence on the union of hydrogen and oxygen. These experiments have led to negative results. By the use of a new method of preparing very pure hydrogen and oxygen, namely, by the electrolysis of a solution of very pure barium hydroxide, the author has succeeded in preparing these gases so pure and dry that tubes containing them can be heated to redness without union of the gases, whilst tubes containing the undried gases, heated side by side with the dried tubes, readily explode. On the introduction of a small quantity of distilled water into the dried tubes, explosion follows at once. In gases which had been allowed to stand for two days only in contact with distilled phosphorus pentoxide, only a slow combination took place, so slowly that in one case ten minutes' heating in the flame of a Bunsen burner caused the union of only one-third of the partially dried gases. It seems therefore that water is not the only determining factor in the explosion of the heated mixture. In order to see if a still higher temperature would bring about the union, coils of very pure silver wire were heated by an electric current in the dried mixture, when it was found that the silver could be heated to its melting-point without causing union.

Experiments have also been made with the object of finding out if the moist gases were measurably dissociated whilst the dry gases were not. By a device of Professor Edward Morley's, used for another purpose, gases were sealed up in tubes in which a contraction of less than 1/7000th of their volume could be detected. The gases were dried before their introduction into the tubes by simply passing them through a phosphorus pentoxide tube. They were then left in contact with the pentoxide for six months. No contraction, even to the small extent above noted, could be observed. The gases tested thus

were hydrogen, oxygen, nitrogen, air, and a mixture of hydrogen and oxygen. These tubes were kept in a dark room during the whole period.

It was found that a moist mixture of hydrogen and oxygen united slowly in sunlight, which may perhaps account for some previous failures to get the gases dry enough not to unite. In the first series of experiments above described, the mixed gases were kept in darkness during their contact with the phosphorus pentoxide, lest the action of the drying agent should not be sufficiently rapid to cope with the water being produced by their union.

*25. "Enzyme Action." By A. J. BROWN.

The author has already shown (*Trans.*, 1892, lxi., 380) that in alcoholic fermentation a constant weight of sugar is decomposed in unit time by a constant amount of yeast in solutions of equal volume containing different amounts of sugar, and has called attention to the fact that in this respect the action of fermentation differs essentially from that of inversion, which, according to C. O'Sullivan and Thompson (*Trans.*, 1890, lvii., 856), follows the law of mass action. At the time the author described his work, the phenomenon of fermentation was believed to be a life function inseparable from the living cell, and therefore it did not appear remarkable that the order of progression of its action should differ from that of inversion; but since Buchner has shown that fermentation, like inversion, is an enzyme action, this point of difference required further investigation, as the simple mass action of invertase demonstrated by O'Sullivan and Thompson is often regarded as typical of all forms of enzyme action.

The author has examined the action of invertase on cane-sugar, and finds that the velocity of its action differs essentially from that of a mass action, and resembles that of fermentation. The velocity of its action represented graphically approximates a straight line when not influenced by the accumulation of inversion products. The retarding influence of inversion products occasions the curve found by O'Sullivan and Thompson, and these authors were mistaken in regarding the curve as the logarithmic curve of mass action. In a true mass action the value K , derived from the expression $K = \frac{1}{\theta} \log \frac{1}{1-x}$,

for any point of the action is a constant, but this is not the case in inversion changes in which the products of inversion accumulate. On the contrary, for such changes the value $2K$ is nearly constant when derived from the expression, recently suggested by Henri (*Comptes Rendus*, 1901, cxxxiii., 891), $2K = \frac{1}{\theta} \log \frac{1+x}{1-x}$,—an expression differing essentially from that representing the progress of a mass action.

But although the action of inversion does not follow the law of mass action, it cannot be independent of mass influence, and therefore the effect of mass during inversion change must be restricted by some other influence. This influence the author believes to be due to the existence of time as a factor in the complex changes which probably accompany inversion.

In any simple chemical change the influence of mass regulates the number of molecular contacts between acting and reacting molecules in unit time; but if a time factor enters into a molecular reaction there must be a point beyond which the number of molecular changes cannot increase owing to the restriction of time in the action, and this point will be determined by the relative frequency of molecular contact and the relative length of the time interval of molecular change. There is good reason to believe that during the inversion of sucrose, this sugar enters into molecular combination with invertase previous to change, which presupposes a complex change and the existence of a time factor of some magnitude. Under these conditions it therefore appears more probable that this factor limits the effect of mass action in inversion changes in solutions of ordinary concentration. But if

this is so, there must be a point of dilution in cane sugar solutions when invertase, acting in the dilute solutions, should exhibit an order of change in conformity with simple mass action. The author shows by direct experiment that this point is reached in a solution containing about 1 per cent of cane-sugar, so far confirming the conclusion that a time factor accompanying molecular change limits the action of inversion in all but very dilute solutions of cane-sugar.

The action of alcoholic fermentation follows the same order of progression as that of inversion, and the work of Kastle and Loevenhart (*Amer. Chem. Journ.*, 1900, xxiv., 491) indicates that the action of lipase progresses in the same manner—it therefore appears probable that both these enzyme actions are regulated, like inversion, by a time factor. With regard to the actions of such enzymes as diastase, glucase, and peptase there is not at present sufficient evidence on which to base an opinion.

*26. "On the Velocity of Hydrolysis of Starch by Diastase with some Remarks on Enzyme Action." By H. T. BROWN and T. H. GLENDINNING.

The rate of change during the hydrolysis of starch by diastase does not conform to the simple logarithmic law of a unimolecular reaction. Throughout the hydrolysis there is a steady augmentation of the coefficient of velocity; in other words, within any given time interval there is more of the residual substance hydrolysed than there should be according to the logarithmic formula.

The results are in the wrong direction to be accounted for by a gradual accumulation of the products of change with a consequent tendency to chemical reversion, nor can they be explained by the intermediate products of change exhibiting a differential resistance to hydrolysis.

If the time curves expressing the rate of hydrolysis of a 3 per cent solution of soluble starch are critically examined, it is found that up to a hydrolysis of 30 to 40 per cent the amount of transformation is very nearly a linear function of the time. A further analysis of the curve shows that the remainder is approximately logarithmic.

In all essentials, the progress of the hydrolysis of starch coincides with that of the inversion of cane-sugar by invertase, as shown by Adrian Brown in the previous paper. The rate of hydrolysis also conforms closely with the empirical formula of Henri for the inversion of cane-sugar.

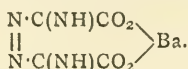
The authors are inclined to adopt a somewhat different explanation of the time curves of hydrolysis from that suggested by Adrian Brown, and one which does not postulate any difference in the time intervals between the successive stages of the reaction other than those due to variations in the respective masses of the reacting substances existing in unit volume.

This hypothesis has been fully elaborated, and an attempt is also made to link the phenomena of enzyme hydrolysis with those of acid hydrolysis, the water ions, or the active dissociated water molecules, being in both cases regarded as the true hydrolysts.

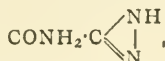
*27. "Polymerisation Products from Diazoacetic Ester." By O. SILBERRAD, Ph.D.

In this research, which is a continuation of work already published (Hantzsch and Silberrad, *Ber.*, 1900, xxxiii., 58), the polymers of diazoacetamide are dealt with. The investigation has led to the discovery of a third series of polymeric products from diazoacetic ester, of which the most stable representative appears to be the amide. This compound, which was formerly known as "pseudodiazoacetamide, $C_3HN_4(NH_2)(CONH_2)_3$," is now shown to be imidoazoacetamide, $NH:C(CONH_2)_2:N:N:C(CONH_2)_2NH$. Its constitution has been established chiefly by a comparative study of the action of reagents on this compound and on its isomerides in the other two series of polymeric derivatives of diazoacetamide, namely, the C- and N-dihydrotetrazinedicarboxylamides, the latter of which has been prepared for the first time. Of the reactions studied,

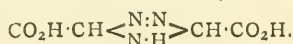
that with alkalis may be taken as characteristic. In the case of the *C*- and *N*-dihydrotetrazinedicarboxylamides saponification occurs in a perfectly normal manner; neither substance shows any inclination to form salts as imidoazoacetamide does. In the presence of mercury, however, *N*-dihydrotetrazinedicarboxylamide forms a compound of such stability that prolonged boiling with concentrated sodium hydroxide entirely fails to saponify the amide. With pseudodiazoacetamide an imido-salt of the amide is first produced, as, for example, the ammonium salt $\text{NH}_4\text{C}(\text{CONH}_2)\text{N}:\text{N}:\text{C}(\text{CONH}_2)\text{N}(\text{NH}_4)$. It was the analysis of these salts which first showed the compound to be a dimolecular polymer of diazoacetamide. Secondary reactions subsequently occur thus (1) Baryta water on warming produces barium imidoazoacetate—



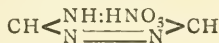
(2) The prolonged action of aqueous ammonia at ordinary temperatures gives rise to isodiazoacetamide,—



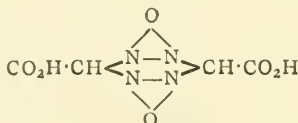
together with a small quantity of diazoacetamide. The constitution of the former was deduced chiefly from its action on benzaldehyde, with which it forms benzalazine, $\text{N}_2(\text{CHC}_6\text{H}_5)_2$. (3) Concentrated sodium hydroxide at 100° gives rise to bisdiazoacetic acid,—



The action of nitric oxide is also worthy of note as by its means either triazole nitrate,—



(a derivative of *N*-dihydrotetrazine), or bisazoxyacetic acid,—

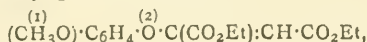


(a derivative of *C*-dihydrotetrazine), can be obtained at will.

28. "Condensation of Phenols with Esters of Unsaturated Acids." Part VII. By S. RUHEMANN.

Benzo-1:4-pyrone (chromone) and its homologues have basic properties: they dissolve in hydrochloric acid to form hydrochlorides, and these solutions yield platinichlorides; but the salts are unstable, and are decomposed by water with re-formation of the benzopyrones.

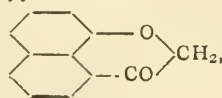
The author having been unable to obtain hydroxybenzo-1:4-pyrones from the dihydric phenols, has attempted to prepare them by starting from their monoethers, and from guaiacol and ethyl chlorofumarate has obtained ethyl guaiacoxymumarate,—



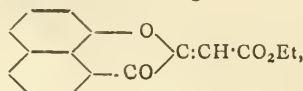
a yellow oil, b. p. 212—213° (at 15 m.m.) and the corresponding acid (m. p. 138° with decomposition); on treatment of this acid with strong sulphuric acid a compound was obtained which is most probably methoxybenzo-1:4-pyronecarboxylic acid. This the author intends to transform into *O*-hydroxybenzo-1:4-pyrone.

It was further shown that the action of ethyl chlorofumarate on α -naphthol differs from the behaviour of the ester towards β -naphthol, for whilst with the latter it yields ethyl β -naphthoxyfumarate, $\text{C}_{10}\text{H}_7\text{O} \cdot \text{C}(\text{CO}_2\text{Et})\text{CH} \cdot \text{CO}_2\text{Et}$, a yellow, fluorescent oil, b. p. 240—242° (pressure 12 m.m.), which on hydrolysis is transformed into the corresponding acid, yellowish plates, m. p. 236° with decomposition, it reacts with α -naphthol to form in addition to a small

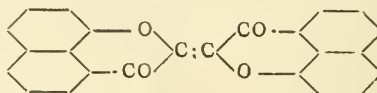
quantity of ethyl α -naphthoxyfumarate, two substances which belong to a new class of compounds. One has the formula $\text{C}_{16}\text{H}_{12}\text{O}_4$, and crystallises in yellow needles, m. p. 146—147°; the other has the formula $\text{C}_{24}\text{H}_{12}\text{O}_4$, it forms orange needles which do not melt at 335°, are insoluble in the ordinary solvents, but dissolve in boiling nitrobenzene. The first compound is regarded as a derivative of the type—



called *naphtharone*, and as having the constitution—



ethyl naphtharonylacetate, whilst the compound $\text{C}_{24}\text{H}_{12}\text{O}_4$ is represented by the formula—



and termed *bisnaphtharonyl*.

Reasons for assigning these constitutions, and the description of some derivatives of these compounds, were given by the author.

29. "The Chemical Change produced by the Immersion of Lead in Distilled Water." By F. CLOWES, D.Sc.

The author finds when very pure lead and ordinary distilled water were employed that much of the lead which underwent change passed into solution most probably as hydroxide, and was removable to a large extent from solution by passage through filter-paper, from which it could again be entirely extracted by cold acetic acid. The compound of lead which remained undissolved by the water was found to have the formula $3\text{PbCO}_3 \cdot \text{PbH}_2\text{O}_2$.

In order to ascertain the respective parts played by atmospheric oxygen and carbon dioxide in solution, distilled water freed from dissolved gases by boiling was employed. When such water was placed in contact with lead in a vacuum or in an atmosphere of hydrogen, action only took place to the extent of 0.3 part of lead per million of water. When the water employed had been boiled in glass vessels and again exposed to air it never regained its full activity. This inhibitive effect varied with different glass vessels, being most marked in those kinds of glass which gave most dissolved matter to the water; contact of cold water and glass did not produce this effect, which was eliminated, however, in the experiments, the results of which are given below, by boiling the water employed in copper vessels.

The average results, expressed as percentages of lead in terms of the water employed, are shown in the following table:—

	24 hours.	48 hours.	72 hours.
Oxygen alone	0.013	0.023	0.029
Carbon dioxide alone	0.005	0.008	0.017
Equal volumes of carbon dioxide and oxygen	0.003	0.003	0.003
Eight volumes of oxygen to one volume of carbon dioxide	0.015	0.018	—

This shows clearly that oxygen is the principal and primary agent, and that carbon dioxide exerts a restraining action in proportion to the volume present. It was found that carbon dioxide acted similarly in preventing solution of litharge.

The first action of aerated water apparently consists in oxidation and formation of hydroxide, which is precipitated as hydroxycarbonate by the carbon dioxide. The action is prevented or retarded by the presence of carbon dioxide in the initial stages. Total immersion of the lead also

retards the action in presence of air, although the final result is the same whether the lead be wholly or only partially immersed in water.

Of the substances which prevent this action, sulphuric acid and soluble sulphates are most effective, soluble carbonates are less so, whilst calcium hydroxide is still less so, but when present in larger quantity actually promotes the action.

30. "The Bases Contained in Scottish Shale Oil." Part I. By F. C. GARRETT and J. A. SMYTHE.

The authors are continuing the examination of the bases contained in the Broxburn shale oil, of which a short account has been already given (*Proc.*, 1900, xvi., 190), and have completed the investigation of the portion boiling below 164°. The following bases have been isolated and identified:—

Pyridine, b. p. 115–116° (in very small quantity).

α -Picoline, b. p. 129°5 (bar. 763 m.m.).

$\alpha\gamma$ -Dimethyl pyridine, b. p. 159–159°5°.

$\alpha\beta'$ -Dimethyl pyridine, b. p. 154–155°.

$\alpha\alpha'$ -Dimethyl pyridine, b. p. 142°5° (bar. 760 m.m.).

$\alpha\gamma\alpha'$ -Trimethyl pyridine, b. p. 170°5° (bar. 760 m.m.).

$\alpha\beta'$ -Dimethyl pyridine is a colourless liquid with a strong pyridine-like odour; it gives a picrate, m. p. 151–152°; a gold compound, m. p. 156–157°; a platinichloride containing 2 molecules of water, and melting (when anhydrous) at 238° with decomposition; and a mercuri-chloride ($C_7H_9, HCl, 6HgCl_2$) in very small, heavy crystals, m. p. 163°.

31. "Note on 'Liquid Nitrogen Peroxide as a Solvent.'" By P. F. FRANKLAND, F.R.S., and R. C. FARMER, Ph.D.

In the authors' recent communication on "liquid nitrogen peroxide as a solvent" (*Trans.*, 1901, lxxix., 1356), they inadvertently omitted to mention the previous work of Bruni and Berti (*Gazz. Chim. Ital.*, 1900, xxx., [2], 151), of which they were not cognisant at the time.

It is fortunate that, whilst the two papers deal to some extent with the same subject, the experimental results do not to any great extent overlap, but rather supplement each other.

Bruni and Berti concerned themselves principally with cryoscopic measurements, and thus extended the still earlier work of Ramsay (*Trans.*, 1890, lvii., 590), whereas the authors have investigated the electric conductivity and ebullioscopic behaviour of the solutions of a considerable number of different substances in the liquid peroxide, besides making a somewhat extensive examination of the action of the latter on a number of other substances, organic and inorganic.

The cryoscopic and ebullioscopic determinations agree in showing that the liquid peroxide is in many cases a powerfully associating solvent, and it is noteworthy that Bruni and Berti found acetic acid to be associated to triple molecules at the freezing-point of the solvent, whilst the authors' measurements at the boiling-point of the latter only revealed an association to double molecules.

The authors desire herewith to express their regret that the important work of these authors had escaped their attention.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

THE twenty-fourth Annual General Meeting of the Institute of Chemistry of Great Britain and Ireland was held at 30, Bloomsbury Square, London, W.C., on Monday, March 3rd, Professor J. MILLAR THOMSON, LL.D., F.R.S., President, in the Chair.

The ordinary annual business of the Institute was transacted, and the President delivered an Address dealing with the work of the Institute during the past year.

The roll of Members has increased by 36, making the total of 1040 Fellows and Associates at present on the

register, while there are 130 students in course of training at the Colleges and Institutions recognised by the Council of the Institute. The President remarked on the higher percentage of passes in the recent examinations, which he considered pointed to the fact that the thoroughness of the Examinations was more fully realised by those preparing for them.

He also mentioned the establishment of an Examination in Biological Chemistry, by means of which the Council hope to encourage analytical chemists to pursue the study of bacteriology, and thus be able to deal with chemical work involving bacteriological knowledge. The examination is specially suited for such as intend entering the practice of chemistry in its relationship to the chemistry and bacteriology of food, water, sewage, and effluents, and the practical applications of biological chemistry to such industries as brewing, tanning, &c. He called attention to the fact that the Institute held an Examination in Ireland in July last, and that the Council hope in future to arrange for a regular examining centre in Dublin.

During the past year the Council have ceased to recognise the Junior, Second Class, and Lower Grade Professional Preliminary Examinations of various examining bodies, and they have now under re-consideration the subjects which shall be compulsory to persons intending to proceed to the examinations of the Institute.

The Council also reported to the Members that during the past year they had addressed to the Local Government Board, and to various county and borough authorities, communications with reference to the combination of the two appointments of Medical Officer of Health and Public Analyst. It has been pointed out that a public analyst requires special training and experience in analytical chemistry far beyond that which is usually acquired by medical practitioners in the course of their professional education. Also, that where the appointments are proposed to be combined the selection of candidates for both positions is necessarily limited. The Council hold the opinion that under the provisions of the Sale of Food and Drugs Act of 1875, it was intended that the Medical Officer of Health and the Public Analyst for a borough or district should be two distinct persons, inasmuch as the Medical Officer is one of those officers empowered by the Act to submit suspected samples for analysis. The qualifications and examinations of the Institute are accepted by the Local Government Boards for public analytical appointments, and it is the desire of the Council that no lower standard of chemical training and experience than that prescribed by the Institute of Chemistry should be accepted for such important and responsible public appointments as those of Public Analysts under the Sale of Food and Drugs Act.

CORRESPONDENCE.

REGULATIONS FOR MILK AND CREAM.

To the Editor of the Chemical News.

SIR,—In the recommendations of the Departmental Committee appointed by the Board of Agriculture to inquire into and report upon the desirability of Regulations for Milk and Cream, 1901, under (c) it is said—"In calculating the percentage amount of admixed water the analyst shall have regard to the above-named limit of 8·5 per cent of non-fatty milk-solids, and shall further take into account the extent to which the milk-fat may exceed 3·25 per cent."

A case came before one of us many years ago of a milk which looked rich and actually contained over 4 per cent of fat, but which, calculated on the solids other than fat, showed 40 per cent of added water. Some years afterwards this curious case was explained by a country dairy-

man, who said it was quite simple, as the supplier of the milk had skimmed the evening's milk and added the cream to next morning's, with as much water as there was of skimmed milk, which he then had for his calves.

In the recommendations referred to 12 per cent total solids is taken as the minimum, of which 3.25 per cent must be fat; but suppose that a milk had been manipulated in the way shown, and that it contained 12 per cent of total solids, 4 per cent of which was fat, it might still be watered to the extent of 16 per cent.—We are, &c.,

DIXON & BYRN.

Chemical and Assay Laboratory,
97, Pitt Street, Sydney.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 7, February 17, 1902.

Action of Potassium Hydride on Ethyl Iodide and Methyl Chloride. New Preparation of Ethane and Methane.—Henri Moissan.—Potassium hydride reacts on ethyl iodide and methyl chloride by fixing hydrogen on to these compounds and liberating the iodine or the chlorine in the form of a binary compound, the alkaline iodide or chloride. This reaction takes place in a sealed tube between 180° and 200° perfectly regularly, without the deposition of carbon and without the liberation of iodine or chlorine.

Conductibility of Liquid Dielectrics under the Influence of Radium Radiation and Röntgen Rays.—P. Curie.—The author proves that the rays emitted by radium and also Röntgen rays act on liquid dielectrics in the same way as they do on air, communicating to them a certain electric conductivity. The apparatus by which this is experimentally demonstrated is described and drawn. In the case of both forms of radiation results of the same order of greatness were obtained. The liquids examined were—Carbon disulphide, petrol ether, amylene, chloride of carbon, benzine, liquid air, and vaseline oil.

Praseodymium Chloride.—Camille Matignon.—The author first determines the principal physical constants of praseodymium chloride by a series of experiments on its progressive desiccation in a current of hydrochloric acid gas. He next proves the existence of a new hydrate of the chloride, $\text{PrCl}_3 \cdot \text{H}_2\text{O}$, and finally gives a simple method of preparation of the anhydrous chloride. The chloride of praseodymium and neodymium when examined together present no marked difference in their properties which could be utilised for fractionation in order to separate them.

MISCELLANEOUS.

Some Platino carbon Compounds.—W. Prandl and K. A. Hofmann.—A solution of chloroplatinic acid in oxide of mesityl is left, *in vacuo*, over caustic soda; after about a fortnight a crystalline mass is formed, blackened by platiniferous products, and hydrochloric acid is given off. The crystals are washed with a mixture of acetone and ether, and re-crystallised in boiling acetone. Pale yellow needles are formed, very soluble in acetone, slightly soluble in ether, and soluble in cold water; this latter solution decomposes spontaneously. The composition of the product is $\text{PtCl}_2 \cdot \text{C}_6\text{H}_{10}\text{O}$; it is identical with the *acechloroplatinum*, obtained by Zeise, by reacting with PtCl_4 on acetone (*Ann. f. Prakt. Ch.*, vol. xx., p. 193). If we boil PtCl_6H_2 with chloroform for several days, hydrochloric acid is given off, and a thick brown residue

is left, covered with a yellowish liquid. This latter was evaporated, then taken up with ether, the solution was filtered and evaporated, and again taken up with ether; then, on evaporation, we obtained pale yellow needles, which were crystallised in warm toluene. The substance answers to the formula $\text{PtCl}_2 \cdot \text{C}_6\text{H}_4$; it is not deliquescent, is stable when exposed to light; when heated to about 140° it commences to decompose.—*Berichte*, vol. xxxiii., p. 2981.

The Ketones of Anthracene.—E. Lippmann and P. Keppich.—It is known that the property of a quinonic oxygen of reacting with hydrochlorate of hydroxylamine is diminished when the two atoms of hydrogen in the ortho-position are replaced by alcoholic residues or by the halogens; it is also known that tetra- and penta-methylphloroglucine are indifferent with regard to phenylhydrazine and hydroxylamine, and that the benzoic and meso-anthracene carbonic acids substituted in ortho, do not give, according to Victor Meyer's law, any ether by the action of alcohol and hydrochloric acid. Having regard to all these observations, it might be supposed that when we replace an atom of hydrogen placed in the meso-position by an acid residue, in the molecule of anthracene, the formation of hydrogenes and oximes would be hindered by the neighbouring position of the two atoms of carbon in the lateral benzenic radical. The researches of the authors on this subject have confirmed this supposition. They describe their method for the preparation of anthraphenone; they then describe its oxidation and reduction. They have also prepared nitro-anthraphenone, as well as tribenzoylanthracene and its tetrahydrogenised derivative.—*Berichte*, vol. xxxiii., p. 3086.

MEETINGS FOR THE WEEK.

MONDAY, 17th.—Society of Arts, 8. (Cantor Lectures). "Photography applied to illustration and Printing," by J. D. Geddes, F.R.P.S.

TUESDAY, 18th.—Royal Institution, 3. "Recent Researches on Protective Resemblance, Warning Colours, and Mimicry in Insects," by Prof. E. B. Poulton, M.A., Hon. LL.D., D.Sc., F.R.S.

WEDNESDAY, 19th.—Society of Arts, 8. "Electric Traction—London's Tubes, Trams, and Trains," by J. Clifton Robinson, Assoc. Inst. C.E., M.I.E.E.

Chemical, 5.30. "The Absorption-spectra of Metallic Nitrates" (Part I.), by W. N. Hartley. "A Method of Determining the Ratio of Distribution of a Base between two Acids," by H. M. Dawson and F. E. Grant. "On the Molecular Complexity of Acetic Acid in Chloroform Solution," by H. M. Dawson. "On the Existence of Polyiodides in Nitrobenzene Solution," by H. M. Dawson and R. Gawler. "Nitrogen Chlorides containing the Propionyl Groups," by F. D. Chattaway. "Derivatives of α -Aminocamphoroxime," by A. Lapworth and A. W. Harvey. "Preparation of Sulphamide from Ammonium Amidosulphite," by E. Divers and M. Ogawa. "Hypiodous Acid," by R. L. Taylor.

Microscopical, 8. Exhibition of Foraminifera, by A. Earland.

THURSDAY, 20th.—Royal Institution, 3. "Caricature in and out of Parliament," by E. T. Reed.

FRIDAY, 21st.—Royal Institution, 9. "Recent Developments in Colouring-matters" (in English), by Geheimrath Professor Otto N. Witt, Ph.D., F.C.S., of Berlin.

SATURDAY, 22nd.—Royal Institution, 3. "Some Electrical Developments," by Lord Rayleigh, F.R.S., &c.

INSTRUCTION IN PURE CULTIVATION OF YEAST, According to Hansen's Methods.

Courses for Beginners, as well as for Advanced Students, in Physiology and Technology of Fermentations. Biological Analysis of Yeast. The Laboratory possesses a numerous collection of yeasts brewers', distillers', wine, disease yeasts, moulds, and bacteria.

Manuals: E. Chr. Hansen, "Practical Studies in Fermentation," London (Spon), 1896. Alfred Jörgensen, "Micro-Organisms and Fermentation," London and New York (Macmillan and Co.), 1900.

The Laboratory supplies for direct use: Cultures of yeast for breweries, distilleries, wine manufactories, &c.

Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V.

THE CHEMICAL NEWS.

VOL. LXXXV., No. 2208.

NOTE ON THE ANOMALOUS DISPERSION OF SODIUM VAPOUR.*

By W. H. JULIUS, Professor of Physics in the University of Utrecht.

THE importance of the study of anomalous dispersion in gases, both for testing dispersion theories, and for investigating the connection of the subject with solar physics,† has induced Professor R. W. Wood to publish a highly interesting paper on the anomalous dispersion of sodium vapour.‡

In most of his experiments, Wood deals with a much denser vapour than I had studied; this may be the reason that he believes he finds a difference between his views and mine about a point on which, in fact, we do agree.

On p. 160 (*loc. cit.*), Wood describes the spectrum of electric light that has passed through a tube containing sodium vapour of increasing density, and how in a few seconds the vapour becomes so dense that total absorption of all the light between the D-lines occurs. Then he says:—"Julius expresses the opinion that this disappearance of the light between the lines is only a result of the strong dispersion"; and he is of a different opinion. This, however, proves, I fear, that he really did not read my paper rightly, as he suspected might be the case (*loc. cit.*, p. 169).

Indeed, speaking of the difference in the result obtained by Becquerel and by myself in studying the dispersion caused by a sodium flame, I suggested (*Roy. Acad. Amsterdam Proc.*, p. 578) that "perhaps Becquerel's flame contained more sodium than mine"; for I felt sure, that in a sufficiently dense vapour the absorption would extend over a broader region of the spectrum. Some lines further, alluding to the absence, in the spectrum, of the light that is strongly deflected by anomalous dispersion and thus falls outside the spectroscopie, I said:—"Here, then, we have a case where the absorption spectrum of a vapour exhibits broad bands not deserving the name of absorption bands"; and then . . . "It would be worth while investigating in how far the anomalous dispersion can have influenced cases, in which broadening or reversal of absorption-lines have been observed."

So it is quite clear that I did not deny the possibility of getting broad bands by absorption. I have never expressed the opinion, that the disappearance of the light between the D-lines in the absorption spectrum of dense sodium vapour is only a result of the strong dispersion; but I warned against always ascribing the observed dark bands to absorption only.

Wood's recent researches are very important as a contribution to our knowledge of dispersion in general. For the present their bearing on the spectral phenomena exhibited by the light from the chromosphere and from sun-spots, seems not to be so direct, because, most probably, the density of the vapours is much less in the solar atmosphere than in the dispersion tubes used by Wood in his brilliant experiments.

An Important Source of Error during Researches on Diastase.—M. Ernow Pozzi-Escot.—The author's researches on diastase lead him to the conclusion that a certain number of published works on diastases and their localisation in special cells lose some of their value when certain facts with regard to colour reactions of diastases are taken into consideration.—*C. R.*, cxxxiv., No. 8.

* A Paper read before the Royal Society, February 20, 1902.

† W. H. Julius, "Solar Phenomena Considered in Connection with Anomalous Dispersion of Light," *Roy. Acad. Amsterdam Proc.*, vol. ii., p. 575; *Astron. Nachr.*, 3672.

‡ R. W. Wood, "The Anomalous Dispersion of Sodium Vapour," *Roy. Soc. Proc.*, vol. lxix., p. 157.

VALENCY OF OXYGEN AND THE HALOGENS.

By H. STANLEY.

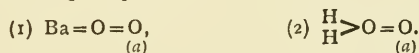
KEKULÉ (*Lehrbuch*, i., 16*) propounded the two principles on which our present theory is based, viz., that carbon is a tetravalent element, and that its atoms have the property of combining among themselves. This latter condition partly accounts for the immense number of carbon compounds. Tilden says:—" . . . Even supposing all the organic compounds completely burnt up, there will still remain a considerable quantity of oxygen. Oxygen is entirely unmatched among the rest of the elements, both as regards the number and varied character of its compounds."

Does oxygen present a case at all analogous to that of carbon?

Heynes has divided the elements into two classes:—(1) Those whose valency is a single number; (2) those whose valency may be represented by a double number.

In the latter class he places oxygen and the halogens. The polyatomicity of these elements seems to come into play chiefly when the atoms of these elements unite among themselves.

Peroxides are divided into two classes. To the first of these belong such bodies as Na_2O_2 or $\begin{array}{c} \text{Na}-\text{O} \\ | \\ \text{Na}-\text{O} \end{array}$; and to the second belong the peroxides of barium and hydrogen—

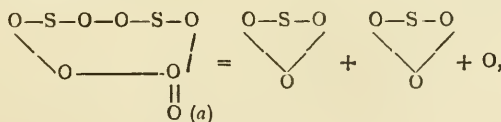


The formula of sulphur dioxide may be written $\text{S} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ and, in analogy with this, we may write ozone as the corresponding oxygen compound, $\text{O} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$. This is a sym-

metrical arrangement, and represents each O atom standing in the same relation to the rest of the molecule. The fact that ozone readily decomposes when heated lends strong support to such a formula as $\text{O}=\text{O}=\text{O}$, (a) (a)

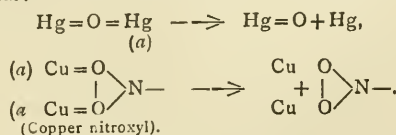
where one of the atoms (a) is disengaged on heating, leaving a molecule of oxygen, $\text{O}=\text{O}$. If we compare ozone and hydrogen peroxide, we find that they act both as reducing and as oxidising agents, and the "available" O atom is in each case united to a second O atom, which resumes its normal valency on the breaking down of the molecule.

The decomposition of sulphuric anhydride may be expressed—



and many other similar reactions in which the quadrivalence of oxygen may be assumed.

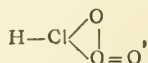
Apparently, however, this high valency of oxygen is not confined to cases of combination between atoms of its own kind, but also when united to other divalent atoms. Thus, for example, take the cases of certain suboxides which decompose on heating, leaving a higher oxide and the metal:—



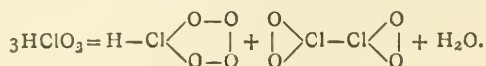
The increasing stability of the series of oxy-acids of

chlorine is probably connected with the quadrivalence of oxygen.

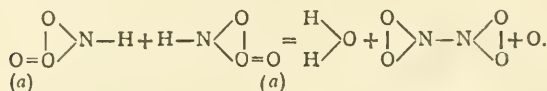
Suppose we write the formula of chloric acid—



its decomposition into perchloric acid and chlorine peroxide may be represented thus:—



Compare with this the decomposition of nitric acid—



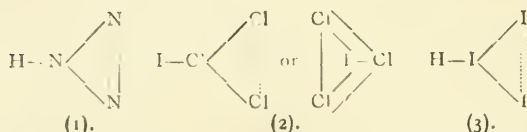
Concentrated HNO_3 boils at 86° and partially decomposes into water, N_2O_4 , and oxygen).

Perchloric acid and its salts are more stable than the chlorates and yield no ClO_2 on heating, but at once evolve oxygen, leaving a chloride.

Oxygen in its dyad capacity in HClO_4 produces a more stable compound than the oxygen in HClO_3 , one of the atoms exhibiting quadrivalence.

Baeyer has, however, recently pointed out that ethyl peroxide may be readily reduced to alcohol and inclines to the opinion that hydrogen peroxide must be represented as HO.OH rather than as O.OH_2 . Collie had previously suggested the formula $\text{Et}_2=\text{O}=\text{O}$ for ethyl peroxide.

The halogens in a tervalent capacity show a marked analogy with nitrogen. Thus we have hydrazoic acid (HN_3), iodine trichloride (ICl_3); and the recent work of Dawson (*Trans. Chem. Soc.*, 1901, 238) plainly points to the existence of such compounds as KI_3 derived from an acid HI_3 . Thus we have—



Many cases in which the halogens are apparently tervalent are known, especially amongst double compounds.

Stortenbeker (*Zeit. Physikal. Chem.*, 1892, x., 183) finds that ICl_3 dissociates into ICl and Cl_2 , the molecular depression (in solutions in glacial acetic acid) decreasing with rise of concentration. This consideration would lend support to the first of the two formulæ given for iodine trichloride above, which then presents analogy with HN_3 and the (as yet) hypothetical acid HI_3 (cf. the decomposition of HClO_4).

The existence of complex molecules of hydrofluoric acid is readily explained if we accept the tervalent character of fluorine, as is also the constitution of the double compounds of the general formula $\text{MF}_{n-1}(\text{NH}_4)\text{F}$ (Poulenc, *Comptes Rendus*, 1892, cxiv., 1426).

It thus seems that oxygen and the halogens (sulphur and possibly other elements) exhibit a valency of a higher order than is normal to them, and that this increase takes place most readily when combinations among atoms of a like kind take place; that the compounds formed by this means are of a lower order of stability than those in which the normal valency is exerted, and that scission takes place in such compounds between the rest of the molecule and that element which is exerting this higher valency. On decomposition taking place, that element resumes its normal atom-fixing power, unless the conditions are such as to cause this power to be still exerted.

Merchant Venturers' Technical College,
Bristol.

THE EFFECT OF SEA-WATER ON MUNTZ'S METAL SHEATHING.

By ERNEST A. LEWIS.

MUNTZ'S metal is a well-known alloy containing from 60 to 62 per cent copper and from 38 to 40 per cent zinc, which has been used for over fifty years for covering the bottoms of wooden ships, and covering piles in harbours, docks, &c. The usual theory assigned for the application of this alloy is that the zinc is slowly and uniformly corroded over the surface by exposure to sea-water, whereby the attachment of barnacles, &c., is prevented.

I have recently had to examine a large number of samples of sheathing which had worn away much too rapidly; some samples had been on piles for only twelve or eighteen months, instead of seven or eight years. The metal in every case became brittle. This peculiar behaviour of the metal is more remarkable because there has been no change in the mode of manufacture, and the metal has to stand bending and tensile tests before leaving the manufactory.

The following are analyses of good sheathing which had been in use some time, and did not show signs of deterioration:—

No. 1.

	Per cent.
Copper.. .. .	61.02
Tin	0.29
Lead	0.567
Iron	0.11
Zinc	38.013

100.000

No. 2.

	Per cent.
Copper.. .. .	61.66
Tin	0.414
Lead	0.94
Iron	0.288
Zinc	36.698

100.000

No. 3.

	Per cent.
Copper.. .. .	60.06
Tin	0.431
Lead	0.922
Iron	0.262
Zinc	38.325

100.000

No. 4.

	Per cent.
Copper.. .. .	61.388
Tin	0.511
Lead	0.436
Iron	0.027
Manganese.. .. .	nil
Arsenic	0.009
Zinc	37.629

100.000

The following are analyses of bad sheathing, which had rapidly deteriorated:—

No. 1a.

	Per cent.
Copper.. .. .	64.704
Tin	0.004
Lead	0.506
Iron	0.055
Arsenic	0.008
Zinc	34.723

100.000

No. 2a.		Per cent.
Copper..	..	66.275
Tin ..	..	traces
Lead ..	..	0.346
Iron ..	..	0.05
Nickel ..	..	0.057
Arsenic ..	..	0.006
Zinc ..	..	33.266

100.000

No. 3a.		Per cent.
Copper..	..	62.006
Tin ..	..	nil
Lead ..	..	0.357
Iron ..	..	0.057
Nickel ..	..	nil
Arsenic ..	..	0.016
Zinc ..	..	37.564

100.000

No. 4a.		Per cent.
Copper..	..	96.562
Tin ..	..	0.021
Lead ..	..	0.099
Iron ..	..	0.01
Zinc ..	..	3.308

100.000

No. 5a.		Per cent.
Copper..	..	92.19
Tin ..	..	traces
Lead ..	..	0.19
Iron ..	..	0.023
Nickel ..	..	0.098
Arsenic ..	..	0.007
Zinc ..	..	7.492

100.000

It will be noticed that, in the samples of good sheathing, the percentages of tin and iron are considerably more than in the bad sheathing. I made a sample of Muntz's metal with chemically pure copper and zinc, and had it rolled and annealed exactly as the metal is manufactured. I then put it in sea-water in an open beaker for a month; the surface became rough, and the sea-water dissolved away some of the zinc.

I also made samples of Muntz's metal containing known amounts of impurity and treated them like the chemically pure metal.

No.	Impurity added.	Appearance after one month.
1.	0.2 per cent tin ..	The surface was smooth.
2.	0.2 „ arsenic ..	„ „
3.	0.2 „ antimony ..	The surface was smooth, but the antimony made the metal brittle.
4.	0.2 „ iron ..	The surface was fairly smooth.
5.	0.2 „ nickel..	The surface was fairly smooth.
6.	0.2 „ manganese.	The surface was smooth.

Muntz's metal consists of two compounds; the one freezes at 894° C., and the other at 460° C. The one freezing at 894° C. is a compound of copper with Cu=Zn, the other is a eutectic alloy of "Cu=Zn+xZn." When Muntz's metal is cast, the "xCu+Cu=Zn" compound solidifies first, and then the "Cu=Zn+xZn" eutectic solidifies; this Cu=Zn eutectic will contain all the impurities originally present in the copper and zinc.

When Muntz's metal is re-heated and rolled, the Cu=Zn eutectic melts and the "xCu+Cu=Zn" compound is raised to the heat at which it is malleable. When

the metal is passed through the rolls, these crystals of "xCu+Cu=Zn" are flattened, and the Cu=Zn eutectic is forced to the edges of the crystals of "xCu+Cu=Zn." When the "xCu+Cu=Zn" cools, it breaks up into very much smaller crystals, which are probably Cu₂Zn.

I have already shown that chemically pure Muntz's metal is easily attacked by sea-water, and that Muntz's metal containing 0.2 per cent tin, arsenic, or manganese is able to resist corrosion much better than the pure metal, and also that Muntz's metal containing 0.2 per cent of iron or nickel is able to resist the corrosive action of the sea-water better than pure Muntz's metal, but not so well as the metal containing 0.2 per cent of tin, arsenic, or manganese.

Lead does not appear to have any influence in making Muntz's metal resist corrosion; every sample of sheathing I have examined has contained from 0.1 to 1 per cent of lead.

Owing to improvements in the manufacture of copper and zinc, these metals are now sold considerably purer than they were years ago; it is now easy to obtain copper of 99.9 per cent purity, and the double distilled spelters contain but traces of impurity.

I believe that Muntz's metal sheathing resists corrosion owing to it containing small amounts of metals as impurities, and that if it does not contain a small proportion of tin, arsenic, iron, manganese, or nickel, it is of no value for ship's sheathing and similar purposes.

In pure Muntz's metal the eutectic alloy of Cu=Zn is comparatively easily attacked by sea-water; the zinc in the Cu=Zn eutectic dissolves away, leaving thin layers of copper, which then forms a galvanic couple with the "xCu+Cu=Zn" compound and rapidly dissolves away the zinc, leaving finally a brittle mass of copper (see analyses No. 4a and No. 5a above).

In a Muntz's metal containing small percentages of tin, arsenic, iron, manganese, or nickel, these metals dissolve in the Cu=Zn eutectic and enable it to resist corrosion for a much longer time, and until the zinc in the Cu=Zn eutectic is dissolved away, the zinc in the "xCu+Cu=Zn" compound is not acted upon.

It has been shown that, in manganese-brasses, steel-metal, Aich's metal, and similar alloys (see "Fourth Report to the Alloys Research Committee of the Institution of Mechanical Engineers"), the iron or manganese added to them dissolve in the lower eutectic and raise its melting-point nearly to the melting-point of the "xCu+Cu=Zn" compound. These metals also have the property of resisting corrosion much better than similar alloys without the iron or manganese, because the Cu=Zn eutectic, when it contains iron or manganese, is able to resist the action of the corrosive liquid for a greater time, thus preventing the formation of minute galvanic couples among the microscopic compounds of the alloys.

ON PYRITE AND MARCASITE.*

By H. N. STOKES.

(Continued from p. 121).

XII. CONSTITUTION OF PYRITE AND MARCASITE; ACTION OF CUPRIC SALTS.

THE importance to chemical geology of an experimental study of the action of copper salts on pyrite and marcasite is self-evident. The following experiments were made, however, with the object of ascertaining whether the method of A. P. Brown (*Proc. Am. Phil. Soc.*, 1894, xxxiii., 225; *CHEM. NEWS*, 1895, lxxi., 179)—namely, heating with neutral copper sulphate solution at 200°—could be used to distinguish these minerals, and incidentally, of testing his hypothesis that the iron in marcasite is wholly ferrous, while that of pyrite is four-fifths ferric. I have therefore confined myself to the conditions of temperature and concentration observed by him.

* From the *Bulletin of the U.S. Geological Survey*, No. 186.

Brown, in his published experiments, has limited himself to titrating the ferrous iron in the resulting solution, while no determination was made of any ferric iron which might be present either in the solution or in the precipitate. As neutral ferric sulphate is practically completely precipitated as basic salt on heating its solution, and as any ferric salt remaining in solution would inevitably be reduced by the sulphides present, it seems reasonably clear that a single experiment with pyrite, in which only the ferrous salt is determined, in which no account is taken of the ferric salt supposed to be formed, and in which no clear evidence of complete decomposition of the mineral is given, can not have great weight in establishing an important hypothesis. While not questioning the correctness of Brown's single observation so far as it goes, I have been wholly unable to obtain the same results.

In each experiment cited below the material was finely ground, carefully freed from oxidation products in the manner employed in my oxidation experiments (p. 63), and about 0.2 grm. heated with 50 c.m.³ of 10 per cent iron-free $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution which had been freed from air by boiling out and cooling in carbon dioxide. The tubes were filled with carbon dioxide, carefully sealed in a current of the same gas, and heated for varying times at 200° C. The filtration and titration with permanganate of the resulting solution were also made in an atmosphere of carbon dioxide, and the end-reaction, which is not very sharp, was determined by comparison with a copper sulphate solution of about the same strength.

Experiments with Cupric Sulphate and Pyrite.

Experiment 1.—Pyrite No. 4. Oxidation coefficient, 60.3. Time of heating, ten hours.

Pyrite taken	0.2024
Ferrous iron in solution ..	0.0305
Total iron in solution ..	0.0314
Total iron in pyrite used ..	0.0944

The solution therefore contains 33.3 per cent of the iron, practically all in the ferrous condition, against 20 per cent as required by Brown's hypothesis. The precipitate was red-brown. In a separate experiment the red substance was found to be left behind on oxidising the sulphide with dilute nitric acid, and proved to be ferric oxide or a very basic sulphate. It is easily soluble in hot dilute hydrochloric acid, and can thus be separated from the sulphide and determined.

Experiment 2.—Pyrite No. 5. Oxidation coefficient, 60.8. Time of heating, eleven hours.

Pyrite taken	0.2028
Ferrous iron in solution ..	0.0510
Total iron in solution ..	Same
Total iron in pyrite used ..	0.0946

The solution contains 53.9 per cent of the iron, all in the ferrous state. The ferric oxide in the red-brown precipitate was extracted by boiling ten minutes with dilute hydrochloric acid in a current of carbon dioxide, whereby some copper also dissolved. The ferric iron thus determined was 0.0272 grm. The final residue, oxidised with aqua regia, gave much iron, which must have come from undecomposed (or imperfectly decomposed) pyrite. From the sum of the two irons above determined it appears that 82.7 per cent of the pyrite was decomposed, and that this portion gave—

62.5 per cent ferrous iron.
34.8 per cent ferric iron.

Required by Brown's hypothesis, 20 per cent ferrous iron

Experiment 3.—Pyrite No. 5. Time of heating, seven hours.

Pyrite used	0.2027
Ferrous iron in solution ..	0.0527
Total iron in solution ..	0.0523
Total iron in pyrite used ..	0.0945

The solution therefore contains 55.3 per cent of the iron entirely as ferrous salt. The ferric oxide, extracted as

above from the red-brown precipitate, was equivalent to 0.0225 grm. iron. The final residue contained much iron. From these data it follows that 79.1 per cent of the pyrite was decomposed, the dissolved portion giving—

69.9 per cent ferrous iron.
30.1 per cent ferric iron.

Required by Brown's hypothesis, 20 per cent ferrous iron.

Experiments with Cupric Sulphate and Marcasite.

Experiment 4.—Marcasite No. 10. Oxidation coefficient, 17.4. Time of heating, seven hours.

Marcasite used	0.2052
Ferrous iron in solution ..	0.0559
Total iron in solution ..	0.0562
Total iron in marcasite used ..	0.0961

After extracting the red-brown precipitate as above, the residual sulphide was found to be free from iron, indicating complete decomposition of the marcasite. From these data it follows that the marcasite yielded—

58.2 per cent ferrous iron.
41.8 per cent ferric iron.

Required by Brown's hypothesis, 100 per cent ferrous iron.

Experiment 5.—Marcasite No. 10. Time of heating, fourteen hours.

Marcasite used	0.2096
Ferrous iron in solution ..	0.0651
Total iron in solution ..	Same
Ferric iron from precipitate ..	0.0318
Total iron in marcasite used ..	0.0977

The precipitate further yielded to hydrochloric acid 0.0626 grm. copper, which was present either as cuprous oxide or as metallic copper, while the final residue was free from iron, showing that complete decomposition had been effected. The above data give for this experiment—

66.6 per cent ferrous iron.
33.4 per cent ferric iron.

Required by Brown's hypothesis, 100 per cent ferrous iron. The copper sulphide remaining after extraction with hydrochloric acid contained 0.2309 grm. copper, from which it follows that two atoms of copper are precipitated as sulphide from each atom of iron dissolved. This necessarily implies a reduction of the copper to the cuprous condition, and a corresponding oxidation of a portion of the ferrous salt or of the sulphur, or of both. That cupric salts can accomplish both of these results is shown in the two following experiments.

(To be continued).

Royal Institution.—The following are the lecture arrangements at the Royal Institution, after Easter:—Dr. Allan Macfadyen, three lectures on "Recent Methods and Results in Biological Inquiry"; Prof. F. York Powell, three lectures on "English Kings and Kingship"; Professor Karl Pearson, three lectures on "The Laws of Heredity, with Special Reference to Man" (the Tyndall Lectures); Professor Dewar, three lectures on "The Oxygen Group of Elements"; Dr. A. Smith Woodward, three lectures on "Recent Geological Discoveries"; Mr. M. H. Spielman, three lectures on "Contemporary British Sculpture"; Mr. W. H. Cummings, three lectures on "British National Song" (with musical illustrations); Professor Walter Raleigh, three lectures on "Poets and Poetry"; and Professor Brander Matthews, three lectures on "The Development of the English Drama"—(1) The Art of the Dramatist; (2) The Drama of The Middle Ages; (3) The Drama under Elizabeth. The Friday Evening Meetings will commence on April 11th, when Professor Dewar will deliver a discourse on "Problems of the Atmosphere." Succeeding Friday Evening Discourses will be delivered by Sir John H. A. Macdonald, Dr. J. Mackenzie Davidson, Sir Robert Ball, Sir Benjamin Baker, Professor A. E. Tutton, and other gentlemen.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 6th, 1902.

Dr. DIVERS, F.R.S., Vice-President, in the Chair.

MESSRS. W. G. Black, L. V. Turner, and H. Lucas were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Samuel Ashe, The Adelaide Hospital, Dublin; Arthur James Cooke, 167, Richmond Road, Hackney, N.E.; Henry Arthur Dobson, Paisley Street, Orange, N.S.W.; James Kewley, King's College, Cambridge; Alexander Macknight, Brucefield, Whitburn, N.B.; William Harrison Martindale, 10, New Cavendish Street, W.; John Wicliffe Peck, 28, West Ella Road, Harlesden, N.W.

The list of names of those recommended for election as Officers and Members of Council was read.

Of the following papers, those marked * were read:—

*32. "The Slow Oxidation of Methane at Low Temperatures." By W. A. BONE and R. V. WHEELER.

The authors have studied the slow oxidation of methane at temperatures between 300° and 400° in a supply of oxygen just sufficient to burn the carbon to carbon monoxide. The method adopted consisted in sealing mixtures of two volumes of methane and one volume of oxygen in bulbs of boro-silicate glass, which were maintained at constant temperatures of 300°, 325°, 350°, and 400° for periods of time varying from one day to three weeks. The bulbs were afterwards examined and a careful analysis of the resulting mixture made.

The results indicate—(1) That the disappearance of the oxygen is accompanied by a proportionate diminution in the volume of the cooled products, due to formation of water; (2) that at no stage of the process is either free hydrogen or free carbon liberated; (3) that a portion only of the methane is burnt, the carbon of which appears as carbon monoxide or dioxide, and the whole of the hydrogen as water; (4) that no other products can be detected at any stage of the oxidation.

Since the interaction of methane and oxygen at these temperatures is a "surface" phenomenon, it is impossible to measure the relative velocities of the reaction at different temperatures, but evidence was obtained that the velocity increases with rising temperature. Thus at 300°, where the velocity is just appreciable, the disappearance of oxygen and formation of water can only be detected after the lapse of one or two weeks. At 400°, on the other hand, the whole of the oxygen always disappeared within a single day, and at 350°, in some instances, in three days.

Experiments have shown that similar bulbs containing electrolytic gas can be maintained at 350° for a week and at 400° for three days, without any visible formation of water occurring; at 400°, in one instance out of three, a marked formation of water took place in a week; in the other two bulbs, however, no change could be detected.

A study of the following possible secondary reactions at 325°, 350°, and 400°, namely (1) $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, and (2) $2\text{CO} + \text{O}_2 = 2\text{CO}_2$, indicates that no complication (moist)

arising from them enters into the methane-oxygen experiments. Further, it has been proved that the following substances do not react at 350–400°, namely, (1) methane and steam, (2) methane and carbon dioxide, (3) carbon and steam.

The authors therefore conclude that the first stage of the oxidation of methane at these temperatures does not consist of a "selective combustion" of either hydrogen or carbon, but in a simultaneous oxidation of carbon and hydrogen, as represented by the equation $2\text{CH}_4 + 3\text{O}_2 = 2\text{CO} + 4\text{H}_2\text{O}$.

The occurrence of carbon dioxide in the products (and in many cases as much as one-third to one-half of the carbon burnt appears as the dioxide) cannot be explained on the supposition that carbon monoxide liberated in the primary oxidation is subsequently gradually oxidised through the agency of steam and oxygen, or steam alone. The more probable explanation is that the carbon monoxide and steam molecules which simultaneously come into being in the primary oxidation are, at the moment of formation, in a very labile and reactive condition, and this would favour the rapid exchange of oxygen in the system $\text{CO} \mid \text{OH}_2 \mid \text{O}_2$. The carbon dioxide is mainly, if not entirely, produced during this short "labile period."

*33. "Isomeric Additive Compounds of Dibenzylketone and Deoxybenzoin with Benzal-p-toluidine, m-Nitrobenzal-aniline, and Benzal-m-nitraniline." Part III. By F. E. FRANCIS, B.Sc., Ph.D.

The additive compounds formed with dibenzylketone and deoxybenzoin with benzal-p-toluidine were unstable, and consequently unsatisfactory for confirming the existence of the so-called α -, β -, and γ -modifications. In the case of dibenzylketone and m-nitrobenzal-aniline the β -modification obtained by re-crystallisation of the α -form from benzene containing traces of piperidine melted 31° higher, and with dibenzylketone and benzal-m-nitraniline 43° higher than the α -additive product; in the latter case, there was also a distinct change in the solubility and appearance of the β -form. These were considered satisfactory confirmations of the individuality of the β -modification, because in cases previously investigated the rise in melting-point was never greater than 10–12°, and since the β -modifications were transformed into the α -by means of heat, this small difference in melting-point was not very satisfactory. α -Dibenzylketone benzal-m-nitraniline on re-crystallisation from benzene containing traces of sodium ethoxide appears to be converted into the γ -modification, and the melting-point rises from 134° to 182°3', but this was the only case observed. Substances of much higher melting-point and smaller solubility, and apparently belonging to neither α -, β -, or γ -modifications, were obtained in the case of deoxybenzoin and benzal-p-toluidine, deoxybenzoin and benzal-m-nitraniline, and dibenzylketone and m-nitrobenzal-aniline. These are similar in molecular weight and composition to the isomerides of lower melting-point, and it is interesting to note that whereas dibenzylketone and benzal-m-nitraniline give a pure α -additive compound, deoxybenzoin with the same substance only gives the isomeride of higher melting-point.

DISCUSSION.

Dr. LOWRY asked if it was not possible that one of the three modifications described by the author as the α -, β -, and γ -forms might be a stable mixture of two isomerides and not a single chemical compound. In the case of the three modifications of π -bromonitrocamphor, those melting at 108° and 142° were found to be the normal and pseudo-nitro-compounds respectively, whilst that melting at 126° was only a stable mixture of these two.

Dr. FRANCIS, in reply, said that he had been unable to obtain any evidence that any of the modifications described was a mixture, and that if they were mixed they could be again separated by fractional crystallisation.

*34. "Mesoxalic Semi-aldehyde." By H. J. H. FENTON, F.R.S., and J. H. RYFFEL, B.A., B.Sc.

Chlorine is slowly absorbed by a solution of tartaric acid containing iron in the ferrous state, and the product, after removal of the unaltered tartaric acid, is found to have powerful reducing and other aldehyde properties. With phenylhydrazine, it yields a bright orange precipitate having the composition $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_2$, which is identical in every respect with the osazone obtained by Nastvogel from dibromo-pyruvic acid (*Annalen*, 1888, cexlviii., 85) and by Will from collodion-wool (*Ber.*, 1891, xxiv., 400 and 3831).

A re-investigation, however, proves that the true melting-point of this osazone is $222-224^{\circ}$ instead of the lower number $201-207^{\circ}$, ascribed to it by various authors. This osazone has the constitution $\text{CH:N}_2\text{HPh}\cdot\text{C:N}_2\text{HPh}\cdot\text{CO}_2\text{H}$, and corresponds either to hydroxy-pyruvic acid, tartronic semi-aldehyde, or mesoxalic semi-aldehyde.

With hydroxylamine, however, the dioxime, $\text{CHNOH}\cdot\text{CNOH}\cdot\text{CO}_2\text{H}$, or dioximidopropionic acid, is obtained identical with that prepared by Söderbaum from dibromopyruvic acid (*Ber.*, 1892, xxv., 904) and by oxidation with cupric hydroxide in alkaline solution mesoxalic acid results.

Since the oxidation product is free from chlorine, these facts leave no room for doubt as to the nature of the substance in question, namely, that it is the semi-aldehyde of mesoxalic acid.

Its formation from tartaric acid in the manner above described is due to the initial production of dihydroxymaleic acid, and it may be prepared in a pure state directly from the latter acid by the action of ferric salts. With ferric sulphate or chloride, for example, the change takes place almost quantitatively according to the equation $\text{C}_4\text{H}_4\text{O}_6 + \text{Fe}_2(\text{SO}_4)_3 = \text{C}_3\text{H}_2\text{O}_4 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{CO}_2$.

After removal of the iron salt and free mineral acid, the product is obtained as a thick syrup, which, so far, has not been induced to crystallise. The derivatives and transformations of this aldehyde-acid are being further investigated.

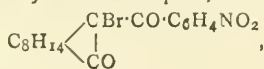
*35. "The Action of Hydrogen Peroxide on Carbohydrates in the presence of Ferrous Salts." III. By R. S. MORRELL and J. M. CROFTS

The specific action of hydrogen peroxide in the presence of ferrous sulphate was first demonstrated by Fenton in the oxidation of tartaric acid to dihydroxymaleic acid (*Trans.*, 1894, lxx., 899). Glucose, lævulose, arabinose, and rhamnose have been shown by the authors to be transformed by this peculiar reaction into osones, which were recognised by their power to react with substituted hydrazines at the ordinary temperature (*Trans.*, 1899, lxxv., 786; and 1900, lxxvii., 1219). It has been found that mannose on oxidation gave an osone which yielded with phenylhydrazine at the ordinary temperature phenylglucosazone. The preparation of pure glucosone from both glucose and levulose has been attempted, and a white amorphous solid has been obtained which gave analytical results agreeing with the formulæ $\text{C}_6\text{H}_{12}\text{O}_6$ and $\text{C}_6\text{H}_{10}\text{O}_6$. This substance reacted readily with phenylhydrazine at the ordinary temperature and furnished a good yield of phenylglucosazone. The glucosone from glucose was feebly dextrorotatory, whilst that from lævulose was slightly lævorotatory. Glucosone obtained by E. Fischer (*Ber.*, 1889, xxii., 87) is lævorotatory.

An aqueous solution of glucosone, prepared from either glucose or lævulose, on oxidation with bromine at 40° furnished a good yield of the calcium salt of a trioxo-butyric acid. The barium salt of the same acid has been obtained, and both the calcium and barium salts seem to be identical with *d*-erythronic acid (*Ruff, Ber.*, 1899, xxxii., 3678). The calcium and barium salts of this acid obtained from glucosone prepared from either dextrose or lævulose have yielded butyric acid on reduction with hydriodic acid and phosphorus.

*36. "m-Nitrobenzoylcamphor." By M. O. FORSTER and Miss F. M. G. MICKLETHWAIT.

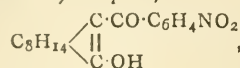
a'-m-Nitrobenzoyl- α -bromocamphor,—



prepared from a'-benzoyl- α -bromocamphor and fuming nitric acid, separates from methyl alcohol in pale yellow flat prismatic needles melting at $93-94^{\circ}$; a 2 per cent solution in chloroform has $[\alpha]_D = +87.9^{\circ}$. m-Nitrobenzoyl- α' -bromocamphor, obtained in a similar manner

from the isomeric benzoylbromocamphor, crystallises in aggregates of small pale yellow needles and melts at $101-102^{\circ}$; a 2 per cent solution in chloroform has $[\alpha]_D = -26.1^{\circ}$.

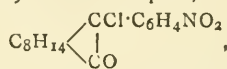
Enolic m-nitrobenzoylcamphor,—



formed on reducing the nitrobenzoylbromocamphors with alcoholic potash, crystallises from alcohol in long pink silky needles melting at $106-107^{\circ}$; it has not been obtained in the ketonic form, but the specific rotation of a 2 per cent solution in chloroform, having $[\alpha]_D = +209.5^{\circ}$ when freshly prepared, falls to $+200.1^{\circ}$ in the course of several days, indicating slight transformation into the isomeride. m-Nitrobenzoylcamphor dissolves in aqueous alkali hydroxides and the alcoholic solution develops an intense purple colouration with ferric chloride; oxidation with potassium permanganate gives rise to camphoric and m-nitrobenzoic acids. The acetyl derivative crystallises from light petroleum in pale brown needles and melts at $127-128^{\circ}$.

Enolic c-nitrobenzoylcamphor crystallises from alcohol in pale brown transparent prisms and melts at 118° ; a 2 per cent solution in chloroform has $[\alpha]_D = +44.5^{\circ}$ when freshly prepared, and $+60.5^{\circ}$ after an interval of several days.

a'-m-Nitrobenzoyl α -chlorocamphor,—



crystallises from alcohol in aggregates of pale yellow prisms and melts at $72-74^{\circ}$; a 2 per cent solution in chloroform has $[\alpha]_D = +40.4^{\circ}$.

a-m-Nitrobenzoyl- α' -chlorocamphor separates from alcohol in small nearly colourless needles and melts at 110° ; a 2 per cent solution in chloroform has $[\alpha]_D = +7.1^{\circ}$. When these isomerides are heated with alcoholic potash, enolic m-nitrobenzoylcamphor is not formed; the sole products are α -chlorocamphor and m-nitrobenzoic acid.

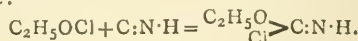
*37. "The Cloëz Reaction." By F. D. CHATTAWAY and J. M. WADMORE.

The reaction between cyanogen chloride or bromide and an alcoholic solution of sodium ethylate appears at first sight to be inconsistent with the nitrogen halogen constitution which we have shown cyanogen chloride and bromide to possess. It becomes intelligible, however, when we consider the behaviour of the nitrogen halogen linkage towards alcohol.

Halogen attached to nitrogen reacts very readily with alcohol, the halogen being invariably replaced by hydrogen and a hypohalogen ester formed thus:— $\text{:N-X} + \text{C}_2\text{H}_5\text{OH} = \text{:N}\cdot\text{H} + \text{C}_2\text{H}_5\text{OX}$.

The interaction of ethyl alcohol and trichloriminocyanuric acid, when ethyl hypochlorite and cyanuric acid are produced, is a simple case. In the Cloëz reaction, cyanogen chloride or bromide first reacts with the alcohol as a typical nitrogen halogen compound, forming hydrocyanic acid and ethyl hypochlorite or hypobromite, thus:— $\text{C:N}\cdot\text{Cl} + \text{C}_2\text{H}_5\text{OH} = \text{C:N}\cdot\text{H} + \text{C}_2\text{H}_5\text{OCl}$.

These then combine and form ethyl iminochlorocarbonate, the hydrocyanic acid, or sodium cyanide, since sodium ethylate is present, behaving as an unsaturated substance:—



The ethyl iminochlorocarbonate then reacts in various ways to form the different substances which have been isolated from the product of the action; for example, it reacts with alcohol to form diethyl iminocarbonate, with water to form urethane, whilst three molecules interact with elimination of hydrogen chloride to produce normal triethyl cyanurate.

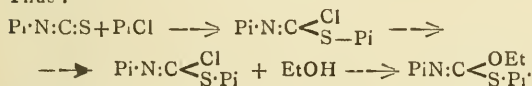
DISCUSSION.

Professor TILDEN thought Dr. Chattaway had brought forward a body of evidence which practically established his case, but he would like to inquire whether the production of a nitrile, by interaction between a common cyanide and a haloid compound, had engaged the attention of the authors, and what explanation they would give of the mechanism of the change. In such interactions, carbon appears to be directly attached to carbon, and there is no evidence of even a temporary formation of a compound in which the cyanide group is linked on by means of the nitrogen.

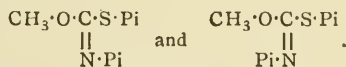
Dr. CHATTAWAY, in reply, stated that the imino-structure of cyanides admitted of action occurring in three ways—addition to the nitrogen, or to both nitrogen and carbon, or to carbon, taking place thus:— $H\cdot N:C + X_2 = HX_2:N:C$; or $H\cdot N:C + X_2 = H\cdot NX\cdot CX$; or $H\cdot N:C + X_2 = H\cdot N:C:X_2$, the mode of interaction in any particular case and the further secondary changes being determined by the nature of the cyanogen derivative, and by that of the substance interacting with it. All reactions of these compounds could be formulated according to one or other of these types. The imino-formulae of the cyanides are capable of expressing conventionally three phases of atomic relationship, the atoms composing a single molecule can only be in one phase at any instant, but the particular phase at which it reacts is determined by a related phase of the interacting molecule.

38. "The Picrimidithiocarbonic Esters." By J. C. CROCKER, B.A.

When picryl chloride is treated with ammonium thiocyanate in alcoholic solution, a reaction readily takes place from which a well crystallised yellow substance is obtained, having the empirical formula $C_{15}H_9N_7SO_{13}$. On hydrolysis, it yields picramide. The reaction may be thus explained. Picryl thiocarbimide, $Pi:N:C:S$, is probably the first product. A molecule of this substance adds on another molecule of picryl chloride, the chlorine atom becoming attached to the carbon atom and the picryl group to the sulphur atom. The acid chloride thus formed reacts with the alcohol to form a picrimidopicrylthiocarbonic ester with the elimination of hydrochloric acid. Thus:—



Similar substances have also been prepared from methyl propyl, and isobutyl alcohols. In the case of methyl alcohol, two substances have been obtained, which are stereoisomeric, corresponding to the "syn-" and "anti-" forms of the oximes—



39. "Robinin, Violaquercetin, Myrticlorin, and Osyritrin." By A. G. PERKIN.

In continuation of the research of which a preliminary account has already been given (*Proc.*, 1901, xvii., 87), the author has re-examined the properties of myrticlorin, $C_{27}H_{28}O_{16}$, a quercetin glucoside present in *Eucalyptus macrorhyncha*, which, as described by H. G. Smith (*Trans.*, 1898, lxxiii., 697), differed mainly from osyritrin (*Proc.*, 1901, xvii., 87) in that the sugar derived from it appeared to be galactose. As Smith (private communication) finds on re-examination that this is dextrose, comparative experiments have been carried out. The results show that myrticlorin is identical with osyritrin.

40. "The Nitration of s-Trihalogen Anilines." By K. J. P. ORTON.

The carefully regulated action of nitric acid on the six s-trihalogen anilines, s-tribromoaniline, 2-chloro-4:6-dibromoaniline, 2:6-dichloro-4-bromoaniline, 4-chloro-2:6-dibromoaniline, 2:4-dichloro-6-bromoaniline, and s-tri-

chloroaniline has been investigated. The anilines were dissolved (or suspended) in glacial acetic acid; to the solution nitric acid free from nitrous acid was added; the mixture, which now contained crystalline aniline nitrate, was heated on the water-bath. From their behaviour when this mixture is heated, the anilines may be sharply divided into two classes, namely, those with a bromine atom in the para-position relative to the amino-group, and those with a chlorine atom in the para-position. With the first, the nitrate of the aniline dissolves quickly, forming an orange solution, which becomes gradually more yellow in colour, and gives off bromine; on cooling, an aniline crystallises out, in which the β -bromine atom has been replaced by a nitro-group; thus, from s-tribromoaniline, 2:6-dibromo-4-nitroaniline is obtained (compare Losanitsch, *Ber.*, 1882, xv., 474); from 2-chloro-4:6-dibromoaniline, 2-chloro-6-bromo-4-nitroaniline (m. p. 177°), and from 2:6-dichloro-4-bromoaniline, 2:6-dichloro-4-nitroaniline are obtained. Secondly, when a chlorine atom is in the para-position, a solution is obtained, transiently of a purple colour, which quickly passes to magenta, and then slowly to a deep crimson. No chlorine or bromine is evolved, nor are anilines detectable in which a bromine atom in an ortho-position or the chlorine atom in the para-position has been replaced by the nitro-group.

During the period of heating there can be isolated from the solutions of both the above classes of anilines a small quantity of the corresponding nitroamines; thus, from s-tribromoaniline is obtained nitroamino-2:4:6-tribromobenzene, slender flesh-coloured needles (from water) melting and decomposing at 143–144°; and from s-trichloroaniline, nitroamino-2:4:6-trichlorobenzene, slender flesh-coloured needles (from water) melting and decomposing at 135°. In solution in acetic acid, in the presence of a trace of a mineral acid, the nitro-amines themselves undergo change, that from s-tribromoaniline yielding 2:6-dibromo-4-nitroaniline, whereas that from s-trichloroaniline yields a characteristic crimson solution. From the crimson solution can be isolated a small quantity of a red crystalline substance, melting and decomposing at 143°. Experiments on the preparation of this and allied substances are now in progress.

41. "Some s-Nitrochlorobromoanilines and their Derivatives." By K. J. P. ORTON.

The following anilines, acetanilides, diacetanilides, and chloroamino-derivatives have been prepared in connection with the investigation described in the preceding communication:—

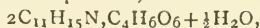
2-Chloro-6-bromo-4-nitroaniline, $C_6H_2ClBr(NO_2) \cdot NH_2$, prepared by chlorinating 2-bromo-4-nitroaniline, long, yellow, prismatic needles melting at 177°; 2-chloro-6-bromo-4-nitroacetanilide, $C_6H_2ClBr(NO_2) \cdot NHAc$, slender, colourless prisms melting at 221–222°; 2-chloro-6-bromo-4-nitrodiacetanilide, $C_6H_2ClBr(NO_2) \cdot NAc_2$, colourless, four-sided prisms melting at 134°; acetylchloroamino-2-chloro-6-bromo-4-nitrobenzene, $C_6H_2ClBr(NO_2) \cdot NClAc$, white lustrous prisms melting at 84–85°; 2-chloro-4-bromo-6-nitroaniline, $C_6H_2ClBr(NO_2) \cdot NH_2$, silky, yellow needles melting at 114°; 2-chloro-4-bromo-6-nitroacetanilide, $C_6H_2ClBr(NO_2) \cdot NHAc$, prepared by nitrating 2-chloro-4-bromoacetanilide, white needles or prisms melting at 194°; acetylchloroamino-2-chloro-4-bromo-6-nitrobenzene, $C_6H_2ClBr(NO_2) \cdot NClAc$, long, pale yellow, lustrous, very soluble prisms melting at 56–57°; 4-chloro-2-bromo-6-nitroaniline, $C_6H_2ClBr(NO_2) \cdot NH_2$, silky, yellow needles melting at 114–115°; 4-chloro-2-bromo-6-nitroacetanilide, $C_6H_2ClBr(NO_2) \cdot NHAc$, prepared by nitrating 4-chloro-2-bromoacetanilide, white prisms melting at 207°; acetylchloroamino-2:6-dibromo-4-nitrobenzene, $C_6H_2Br_2(NO_2) \cdot NClAc$, small, lustrous, four-sided prisms, with domed ends, melting at 110–111°; 2:4-Dibromo-6-nitrodiacetanilide, $C_6H_2Br_2(NO_2) \cdot NAc_2$, prepared by boiling the aniline with excess of acetic anhydride, aggregates of prisms or rhombs melting at 96–97°; 2:3:4:6-Tetrabromoacetanilide, $C_6HBr_4 \cdot NHAc$,

prepared from tetrabromoaniline, silky, white needles melting at $228-229^{\circ}$; 2:3:4:6 tetrabromodiacetanilide, $C_6HBr_4NAC_2$, lustrous, four-sided prisms with domed ends, melting at 164° . 2:3:6 Tribromo 4-nitroaniline, $C_6HBr_3(NO_2)NH_2$, prepared by brominating 3-bromo-4-nitroaniline, pale lemon-yellow needles, melting at $155-155.5^{\circ}$. 2:3:4-Tribromo-6-nitroaniline, $C_6HBr_3(NO_2)NH_2$, prepared from 3-bromo-6-nitroaniline, orange-yellow needles, melting at $165.5-166^{\circ}$; 2:3:4-tribromo-6-nitroacetanilide, $C_6HBr_3(NO_2)NHAc$, colourless, flattened needles melting at 221° .

42. "The Resolution of Pheno- α -aminoheptamethylene into its Optical Isomers. Tartrates of Pheno- α -aminoheptamethylene and of Hydrindamine." By F. S. KIPPING and A. E. HUNTER.

An investigation of the salts produced by the combination of *dl* pheno- α -aminoheptamethylene with tartaric acid has shown that this base behaves quite differently from *dl*-hydrindamine (pheno α aminopentamethylene) in spite of the similarity in constitution of the two bases.

cl-Pheno α -aminoheptamethylene-*d*-tartrate,—



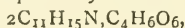
separates from neutral and from acid solutions of the *dl*-base in aqueous tartaric acid, in lustrous prisms decomposing at about 235° ; in aqueous solution $[\alpha]_D = +13^{\circ}$.

l-Pheno α -aminoheptamethylene hydrogen *d*-tartrate, $C_{11}H_{15}N_4C_4H_6O_6 + 3H_2O$, is obtained when the solution of the normal tartrate is mixed with excess of tartaric acid and fractionally crystallised; it forms slender prisms, and melts at $181-182^{\circ}$; its aqueous solutions are feebly laevorotatory ($[\alpha]_D = -1.6^{\circ}$ approximately).

l-Pheno α -aminoheptamethylene *d*-tartrate, $2C_{11}H_{15}N_4C_4H_6O_6$, prepared from the *l*-base, crystallises in transparent, triangular plates, and decomposes at $215-217^{\circ}$. The hydrochloride of the *l*-base forms lustrous prisms, and in dilute aqueous solution its specific rotation is $[\alpha]_D = +24^{\circ}$.

Benzoyl-*l*-pheno- α -aminoheptamethylene, $C_{11}H_{14}N \cdot COPh$, crystallises in needles, melts at $175-176^{\circ}$, and is dextrorotatory in methyl alcoholic solution.

d-Pheno α -aminoheptamethylene *d*-tartrate,—



can be isolated from the mother-liquors obtained after separating the hydrogen salt of the *l*-base; it is anhydrous and decomposes at about $216-217^{\circ}$.

d-Pheno α -aminoheptamethylene hydrogen tartrate, $C_{11}H_{15}N_4C_4H_6O_6$, prepared by treating the normal salt with tartaric acid, decomposes at about $205-206^{\circ}$.

dl-Hydrindamine hydrogen *d*-tartrate,—



crystallises in slender needles, melts at $163-169^{\circ}$, and is not resolved or changed in any way by repeated crystallisation from water. The normal *d*-tartrate of the *dl*-base forms plates melting at about 200° , and dissociates hydrolytically in aqueous solution.

l-Pheno α -aminoheptamethylene *d*-bromocamphorsulphonate, $C_{11}H_{15}N_4C_{10}H_{14}BrO \cdot SO_3H$, crystallises in prisms melting at $216-217^{\circ}$; in dilute aqueous solution $[\alpha]_D = +47.8^{\circ}$.

PHYSICAL SOCIETY.

Ordinary Meeting, March 14th, 1902.

Mr. S. LUPTON, Vice-President, in the Chair.

A PAPER on "The Thermal Expansion of Porcelain" was read by Mr. A. E. TUTTON.

The paper gives an account of experiments made to determine the expansion of Bayeux porcelain between 0° and 180° C. The material employed was a portion of the tube used by Bedford in his experiments on the expansion of porcelain between 0° and 830° C. Another piece of the same tube has also been used by Chappuis in a

series of determinations by the Fizeau method between 0° and 83° C. The author has worked with an interference dilatometer, which possesses advantages over the Abbe form of the original Fizeau apparatus. The observing part of the instrument is separated from the expansion chamber, and the temperature of the interference tripod and the substance under investigation, which it carries, is measured by means of a thermometer bent just above the cylindrical bulb, and so arranged that the latter lies on the tripod table. The chief advantages over the Fizeau apparatus are briefly:—1. The employment of a microscopic method of measuring the position and width of the interference bands. 2. The use of autocollimation. 3. The employment of C hydrogen light. 4. An arrangement of the thermal chamber which readily permits an extension of the range to 120° C. The author has also introduced an aluminium compensator, a relatively thick disc of aluminium laid on the top of the porcelain tube. This overcomes the difficulty of polishing the porcelain, and affords a large field of bands instead of an annular ring showing parts of bands. The mean of three determinations with three specimens of material gives the following result for the linear expansion $L_t = L_0[1 + 10^{-9}(2522t + 7.43t^2)]$. The results presented by the author agree tolerably well with those of Chappuis, but the constant *a* is slightly smaller. The constant *b* is seven times larger than according to Bedford. The discrepancies between the results of Chappuis and Bedford appear to be due to a fundamental real difference, dependent on the interval of temperature for which the determinations were made. The increment per degree of the coefficient of expansion of porcelain is not a constant quantity, but one which is much larger between 0° and 100° than at higher temperatures. The supposition of Prof. Callendar, as to the anomalous expansion between 0° and 100° , appears to be well founded.

The SECRETARY read a letter from Dr. P. E. SHAW stating that the accuracy of the micrometer readings seemed to depend more on the distinctness of the rings than on anything else. He asked if the author considered mercury or hydrogen light better than sodium light, and if the error in the present research was less than $\frac{\lambda}{25}$, which is supposed to represent the accuracy of the Abbe-Fizeau method.

Dr. CHREE expressed his interest in the paper because of its bearing on the measurement of temperature by the gas thermometer, in which case it is essential to know the coefficient of expansion of the porcelain bulb. He did not consider the behaviour of porcelain anomalous, because an irregular expansion might be expected. In the case of Jena glasses used in thermometry, the values of *a* and *b* determined between 0° and 100° are different to those obtained when the range is extended to 200° C. He was surprised at the differences between Bedford and Chappuis and Tutton, and said that the evidence was in favour of the instruments used by the latter observers. It would be interesting if the author could obtain Chappuis's specimen of porcelain, and repeat his experiments between 0° and 80° .

Mr. TUTTON, in reply to Dr. SHAW, said that the bands were perfectly distinct when using red hydrogen light. He did not use mercury light because of the necessity of constantly heating the tube.

The SECRETARY then read a paper by Mr. W. WILLIAMS on "The Temperature Variation of the Electrical Resistances of Pure Metals and Allied Matters."

In the first part of the paper an attempt is made to correlate the periodic variations which pure metals exhibit as regards their atomic weights, chemical valencies, melting-points, and electric resistances. If *m* is the chemical valency, *V* the atomic volume, θ the absolute temperature, *T* the absolute melting-point, and *c*, or $V^{\frac{1}{3}} \alpha T$ the constant of Pictet's law, then $\sigma \propto \frac{mV\theta}{cT}$, where

σ is the specific resistance at 0°C . This relation holds for most of the metals, but fails for gold, indium, tin, and aluminium, and also for metals of the iron group. The temperature resistance-coefficients of pure metals are not equal to $\frac{1}{273}$, and an expression for the change of resistance with temperature has been deduced which holds approximately for many metals. The author also obtains simple expressions for the average increment per degree of the specific heat of metals, and for the ratio between the specific resistances of the solid and liquid states of a metal at the temperature of fusion.

A paper entitled "*A Suspected Case of Electrical Resonance of Minute Metal Particles for Light Waves. A New Type of Absorption*," by Prof. R. W. Wood, was read by the SECRETARY.

Experiments on which the author has been engaged have led him to believe that he has found a new type of light absorption, which it may be possible to refer to the electrical resonance of small metallic particles for waves of light. Metallic deposits on glass have been produced which are shown by the microscope to consist of particles less than the wave-length of light, and which by transmitted light exhibit colours as brilliant as those produced by aniline dyes. The author has sought to explain these colours by interference and diffraction, and has been forced to accept the hypothesis suggested in the title of the paper. The metallic deposits can be obtained by heating small fragments of the alkali metals in exhausted glass bulbs, when the vapour condenses on the cold parts of the bulbs and forms the films. It can be shown that the colours are due to the presence of metallic sodium (in the case in which sodium has been used) by allowing air to enter the bulb; oxidation takes place, and the film vanishes. In some experiments the air has been allowed to enter very slowly, and the changes which the film undergoes before it vanishes have been examined. The particles which form the deposits can be classed under three heads; (1) coarse particles which diffract or scatter light and give the bulb a silky lustre; (2) minute particles very close together which regularly reflect those wave-lengths absent in the transmitted light, but give no scattered light; and (3) minute particles far apart which diffuse light of the same wave-lengths as those which are to some extent absent from the transmitted light. By observing the spectrum of the transmitted light the author has examined the changes in colour which accompany changes in temperature of the films. The paper gives an account of the relation between the colour of the film and the size and distribution of the particles, and also of the behaviour of the films with polarised light. Experiments upon the electric resistance of the films have proved that they are non-conducting. The author concludes by stating that at the present stage it is impossible to decide either in favour of, or against, the theory of resonance. The idea of resonance has proved a useful working hypothesis for explaining some of the phenomena described in the paper.

The SECRETARY read a letter from Prof. R. THRELFALL drawing the attention of the author to some experiments upon the same subject published by him in 1894. Particles of gold and platinum were deposited in a liquid, and good scattering of light obtained in all cases. The polarisation angle was exactly the same as with non-conducting particles. Prof. J. J. Thomson has shown that the peculiar scattering effect is only to be expected within very narrow limits as to size of particles. The colours observed by Prof. Wood should only be noticed when the particles have a very restricted size, and evidence in favour of or against the author's theory should be afforded by comparing the observed and calculated sizes of the particles. The value of the polarisation angle of the scattered light observed by Prof. Wood is evidence in favour of the theory suggested.

The CHAIRMAN pointed out that the experiments had probably been rendered difficult by the different colours in which the oxides of sodium and potassium can exist.

The Society then adjourned until April 11th.

NOTICES OF BOOKS.

Inorganic Evolution as Studied by Spectrum Analysis. By SIR NORMAN LOCKYER, K.C.B., F.R.S., Professor of Astronomical Physics in the Royal College of Science, London, &c. London: Macmillan and Co. 1900. Pp. 198.

THE volume now before us contains an account of some of the author's recent inquiries into the chemistry of the stars, and of some questions which have grown out of these inquiries. He first describes the principles, methods, and application of the inquiry to the sun and stars. One of the first questions that arises is this:—Do the chemical elements make themselves visible indiscriminately in all the celestial bodies, so that practically, from a chemical point of view, the bodies appear to us of similar chemical composition? The answer to this question is in the negative.

From the spectra of those stars which resemble the sun, it is to be gathered that the atmospheres of some stars are chiefly gaseous, consisting of elements we recognise as gases here; others are chiefly metallic, while others, again, are mainly composed of carbon or of compounds of carbon. Three of the main groups of stars may be classified as follows:—

Gaseous stars	Longest spectrum
Metallic stars	Medium spectrum
Carbon stars	Shortest spectrum

and by associating the above with other observations it is reasonable to make the following general statement:—

Gaseous stars	Highest temperature
Metallic stars	Medium temperature
Carbon stars	Lowest temperature

Hence the difference in apparent chemical constitutions are associated with differences of temperature. Laboratory work has enabled the author to bring still a third class of facts into the question, by the help of the clèveite gas-spectrum and the spectrum of enhanced metallic lines, and the results are quite in harmony with the preceding ones:—

Gaseous stars ..	Highest temperature ..	{ Strong clèveite gas, and faint enhanced lines.
Metallic stars ..	Medium temperature ..	{ Feeble clèveite gas, and strong enhanced lines. No clèveite gas, and strong arc lines.
Carbon stars ..	Lowest temperature ..	{ Faint arc lines.

The chemical law, therefore, is this—that in the hottest stars we find, generally speaking, hydrogen, helium, asterium, and doubtless other still unknown elements, almost exclusively. At the next lowest temperatures these gases are being replaced by metals in the state in which they are observed in the laboratory when the most powerful jar-spark is employed. At a lower temperature still, the gases almost disappear entirely, and the metals exist in the state produced by the electric arc.

The author then passes from general to particular results, and gives in detail the results of his observations on stars as hot as, or hotter than Arcturus, this star being taken as representing the temperature of the sun.

The chemical classification of stars is the next point dealt with, but it must be understood that only the most predominant chemical features are considered, and that there is no sharp line of separation between the larger groups.

In 1873 the author suggested that many difficulties would vanish if it were conceded that the "atoms" of the chemist were broken up or dissociated by the high temperatures employed in the new method of investigation.

Some of the views brought forward from time to time have received general acceptance, but the author's view as to the subsequent dissociation of molecules, when once the line spectrum stage has been reached, was still rejected by many. The various points involved are then dealt with *seriatim*, under the headings of Stellar evidence, "Series" evidence, "Shifting" of lines evidence, Magnetic perturbation evidence, and Fractionation evidence.

From the above it is reasonable to suppose that the spectrum of an element is produced not by similar but by dissimilar molecules.

The next phase of the subject considered by the author is the objections raised to the dissociation hypothesis. He has supposed, and he thinks legitimately until the contrary is proved, that the materials out of which, on the nebular hypothesis, worlds are eventually formed are similar in all parts of space, and he contends from stellar evidence that the facts are distinctly against the view of "different chemical parishes in space." The Sun, Arcturus, and Capella, and other cooling stars, enormously separated in space, contain the same spectral lines with almost identical intensities, so that not only do they contain the same elements, but they contain them "in absolutely identical proportion." We are therefore justified in the conclusion that the differences recorded in stellar spectra do not come from a different percentage composition of the elements present, but arise from the action of different temperatures on the same molecules.

The next important point is the discussion as to the distribution of the various chemical groups of stars, not only in their relation to their direction in space as seen from the solar system, but also in relation to their distance from us, and the results arrived at are summarised in Chapter XVII.

It is found that the gaseous stars are chiefly in the Milky Way, and are far away from us; the proto-metallic stars are not so confined to the Milky Way, and they are not so far away from us; but the metallic and carbon stars have not much connection with the Milky Way, and they are close to us. Finally, the author is led to the conclusion that there is no localisation of the chemical elements so far as *direction* is concerned.

The final chapters of this book deal specially with inorganic evolution, and it is argued that as evolution depends upon time in organic, so does it depend upon temperature in inorganic nature.

It is well known that the effect of high temperatures is to produce simplifications of matter; dissociation in all its stages must reveal to us the forms, the coming together of which has produced the thing dissociated or broken up by heat. If this be so, the final products of dissociation must be the earliest chemical form. The earlier chapters of this book answer the question fully; it is shown how in cosmical evolution we deal with a continuity of effects accompanied by considerable changes of temperature, from the gradual coming together of meteoric swarms until eventually we have a mass of matter cold and dark in space. The various stars which represent these changes have been arranged along a so-called temperature curve. On one branch the stars get hotter until at the top we find the hottest stars that are known, then on the descending branch we have the cooling bodies coming down in temperature until we reach that of a dark world, like the companion of Sirius, or our own earth.

The Colouring Matter Industry ("L'Industrie des Matières Colorantes"). By JUSTIN DUPONT, Professor at the "Institut Commercial." With 34 Figures in the Text. Paris: J. B. Baillière and Sons. 1902. Pp. 360.

THE colouring matter industry is one of great importance, not only on account of the enormous development of the allied industries, but also because of the scientific interest which surrounds these products, and the theoretical discussions which are carried on with regard to their con-

stitution. In fact the study of colouring matters now forms a definite branch of chemical science, and the author hopes that this elementary volume on this branch of chemistry will be found useful to those who are studying the subject.

The plan adopted in arranging this book is both simple and logical; after a short review of the general theory of colouring matters, he enters on the subject itself, and divides its treatment into three parts, viz., natural colouring materials, artificial colouring materials, and the application of colouring materials.

The first part gives a full and interesting account of the history, properties, and characteristics of natural dyes.

In part two (which forms the bulk of the volume) the author first deals with the matters extracted from coal-tar, then the intermediary derivatives between them and the actual colouring matters. These chapters contain a great deal of useful information as to the constitution and preparation of many of these intermediary products. He then deals with the colouring matters themselves, and he has adopted the classic divisions by which the colouring materials are divided into a certain number of groups or families, according to their chemical functions. He fully describes the characteristics of each of these series of bodies, their manner of formation, and their properties.

The third part of the volume describes the methods used for the application of colouring matters, and the properties of the principal fibres in connection with which they are used, such as silk, wool, cotton, &c. The wide differences in the properties of these different fibres necessitates the use of special methods for each; these are described in a clear and lucid manner.

The book is furnished with a full table of contents and a good index.

Practical Chemistry. By R. ABEGG and W. HERZ. Translated by H. T. CALVERT, B.Sc. (Vict.). London: Macmillan and Co. New York: The Macmillan Company. 1901.

THE scope and object of this book are indicated by the secondary title "An Experimental Introduction to Laboratory Practice and Qualitative Analysis from a Physico-chemical Standpoint." Such a work as this is a complete novelty in the English language, and the introduction of a considerable amount of theoretical discussion in a practical book is regarded as somewhat unusual, though in our opinion by no means to be deprecated. The early introduction of the theory of ionisation tends to simplify many problems of analytical chemistry, and above all does much to prevent the subject becoming a mere test-tube exercise, though a discussion of the theory in its fullest developments would make too great demands on the student's knowledge. Such books as these, in which the causes of reactions are more emphasised than the visible effects, possess a very distinct value of their own.

The book opens with a short course of preliminary preparations of the most common inorganic substances, followed by a chapter on the theoretical foundations of analysis. Here such subjects as the law of mass action are dealt with and dismissed in a few pages, but as far as they go the accounts appear satisfactory summaries. The section on the reactions of the kations and anions exhibits no great difference from those of the ordinary type of analytical hand-book, except for the continual references to, and explanations by means of, the ionisation theory; in some places the introduction of more formulæ might be advocated, as, for example, in the case of the thio-acids of tin, &c.

The system adopted for the detection and qualitative separation of the elements is based chiefly upon Wallach's analytical tables, but the authors claim that the method of separating the acids is new. This part of the book is particularly well arranged, and the tables of the atomic weights of the elements and the periodic system give the results of the most recent determinations.

Leçons sur la Théorie des Gaz. Première Partie. By L. BOLTZMANN. Translated by A. GALLOTTI. Paris: Gauthier-Villars. 1902.

THESE lessons on the theory of gases are provided with an introduction and notes by M. Brillouin, of the Collège de France. The introduction shortly reviews the historical development of the molecular hypothesis in the theory of gases, and forms a suitable preface to the detailed study of the subject. This volume deals with the molecules considered firstly as elastic spheres, and, secondly, as centres of force, the third chapter being occupied with the investigation of the repulsive force varying inversely as the fifth power of the distance. The law of distribution of velocities, and the mathematical signification of Boltzmann's magnitude H , call forth some valuable criticisms by M. Brillouin, who is not altogether satisfied with some of Boltzmann's conclusions.

This work is adapted for those students of physics, who, having already a fair knowledge of the theory of gases, require a book in which recent work on the subject is collected in convenient form, and attempts made to do something towards the elucidation of some of the many difficulties. Though occasionally the author appears to us somewhat too daring, he is never obscure, and every mathematical step is carefully and precisely worked out.

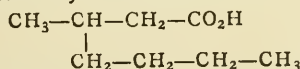
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

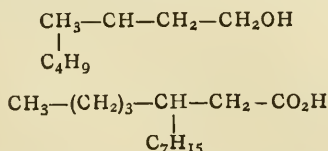
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiv., No. 8, February 24, 1902.

Properties of Azobenzene and Hydrazobenzene.—F. Freundler and L. Béranger.—The authors apply Friedel and Crafts's reaction in the attempt to prepare azoic compounds and their derivatives. They find that this reaction cannot be employed for the preparation of the azoic compounds with ketonic function, and so employ other methods. The diacetylhydrazobenzene can be prepared by heating hydrazobenzene for several hours to boiling point, with excess of acetic anhydride. By using a commercial product very rich in azobenzene they obtain, instead of a diacetyl derivative, a molecular combination of this latter with azobenzene. This substance crystallises without dissociating in large orange-coloured prisms, melting at 98.5–99°. It corresponds to the formula $2[C_6H_5.N(COCH_3)_3].N.(COCH_3).C_6H_5.N=N.C_6H_5$.

Constitution of Dibutyl and Diönanthyl Alcohols.—Marcel Guerbet.—The author has already shown that dibutyl alcohol, $C_8H_{18}O$, can be prepared by heating normal butyl alcohol with its sodium derivative to about 200°. A series of experiments on this substance lead him to attribute to dibutyl alcohol the formula—



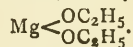
and to dibutyl and diönanthyl alcohols respectively the constitutional formulæ—



The Polymerised State of Ordinary Indigotine and the Isomeric Transformation of Indigotine into Indi-

rubine.—L. Maillard.—The blue of indigo, when extracted by chloroform, cannot be obtained in a crystalline form, and thus differs from indigotine in at least two properties—(1) its much greater solubility in chloroform; (2) the ease with which it is transformed into indirubine by means of acid chloroform. These differences are explained if the two blue colouring matters are considered as polymers the one of the other, and by attributing naturally the most complicated formula to the most stable.

Certain Reactions obtained by means of Magnesium Amalgam.—L. Meunier.—Magnesium amalgam, even in the cold, attacks absolute ethylic alcohol, hydrogen being evolved and the corresponding ethylate separating out. This ethylate, when washed and rapidly dried, is in the form of a white powder, corresponding to the formula—



Magnesium amalgam can also be used for the preparation of the saturated carbides, as it reduces the alcoyl iodides in presence of absolute alcohol. Ethylic aldehyde acts very violently on the amalgam, but the reaction can be moderated by adding anhydrous benzine aldehyde or a sufficient quantity of anhydrous ether. A syrupy liquid is obtained which contains a magnesium compound in solution.

Constitution of Tariric Acid.—M. Arnaud.—Tariric acid is the principal constituent of the glyceride which can be extracted from a certain grain. The author has shown that this acid is an isomer of stearolic acid, and that it can be integrally transformed into stearic acid by the action of hydriodic acid and red phosphorus at 210°. This acid, thus prepared, has a formula $C_{18}H_{32}O_2$, and belongs to the series of non-saturated acids, $C_nH_{2n-4}O_2$. It ought to contain a triple acetylenic liaison like stearolic acid. This latter fact the author proves by a series of experiments on the acid and its salts, and proposes to examine the products of oxidation of the acid.

New Method of Identifying the Pseudo Acids. Application to the Oximido-cyanacetic Ethers.—P. T. Muller.—The oximido cyanacetic ethers are identified by the joint presence of the isonitroso-radicle $=NOH$ and the negative radicle $-CN$, which give to the compounds decided acid properties. The electric conductivity of their aqueous solutions also place these bodies near to acetic acid. They can be accurately titrated against phenolphthalein, and their soda-salts do not show appreciable hydrolysis. Their aqueous solutions are colourless, with a slight yellow tinge, the alkaline salts being yellow both in the solid state and in solution. However, their quarter normal solutions are transparent enough for the refractive power to be measured. A table is given of the optical measurements.

Some Derivatives of Methyl-nonyl-ketone.—H. Carotte.—Continuing his research on the derivatives of methyl-nonyl-ketone, the author transforms this acetone into nitrile-alcohol by fixation of hydrocyanic acid. By immediate hydration of this nitrile-alcohol he obtains the ordinary corresponding acid-alcohol, and in addition an amido-alcohol resulting from the fixation of a single molecule of water on to the alcohol nitrile.

Researches on the Fatty Acids present in Contaminated Waters.—H. Causse.—The presence of fatty acids themselves in water is not injurious, but as a rule it indicates contamination. When their proportion is about 0.05 m.grm. per litre their influence on the water is slight but perceptible. They discolour sulphurous violet slowly and incompletely. Para-diazobenzene-sulphonate of sodium gives a slight yellow colouration, without a trace of orange. If, however, the quantity of fatty acids increases, the oxygen in solution is reduced, and the reactions for pure waters disappear, giving place to those of contaminated waters.

MISCELLANEOUS.

The Variations of Temperature Accompanying the Solidification of Fused Organic Bodies.—Br. Pawlewski.—The author fuses a few cubic centimetres of an organic substance in a test-tube, and plunges a thermometer therein; then, while allowing the substance to cool rather slowly, he observes the thermometer every twenty seconds when near the point of solidification, and plots the figures on a curve in functions of time. According to the character of the curves, he is able to separate the substances examined into three classes. In the first type the ordinate sinks rapidly below the normal point of solidification s (that observed in a capillary tube), then remains constant; it then sinks again so that the two arcs of the curve separated by the median line show opposing concavities. The second type only differs from the first in the suppression of the median line, and gives a curve with no inflection for a temperature below s . In the third type the temperature, after falling considerably below s , rises again very rapidly, and remains constant for some time at a little below s ; the rest of the curve is like that of the first type. Agitation causes substances of the third type to behave like those of the first, by destroying the surfusion. The falls below s are sometimes considerable (41° in the case of acetyldiphenylamine). Isomeric bodies often belong to different types.—*Berichte*, vol. xxxiii., p. 3727.

The Separation of Arsenic.—M. Rohmer.—The method consists in the distillation of the arsenical liquor in a current of hydrochloric and sulphurous acid gases (the latter is to reduce the As_2O_5); the arsenic is then given off as $AsCl_3$, and is collected in a cooled receptacle containing water. Bunsen observed (*Lieb. Ann. Ch.*, vol. cxcii., p. 321) that the reduction of the As_2O_5 is never complete, but the author, when operating in the presence of a little hydrobromic acid, obtained very satisfactory results. The operation is performed in a 500 c.c. flask; the solution to be examined is poured in with an excess of fuming hydrochloric acid, so as to fill one-third of the flask, and 1.5 grms. of potassic bromide or 1 gm. of bromine is added. It is then distilled for about fifteen minutes, while the current of hydrochloric and sulphurous acid gases are being passed through; the solution is thus reduced to about 40 c.c. The fumes are condensed first in a long tube, and then collected in a one-litre flask cooled down to 0° , and containing 300 c.c. of water; finally, the rinsings of the long tube are added to the contents of the flask. The arsenic can be estimated either gravimetrically in the form of As_2S_3 , or volumetrically by means of a titrated solution of iodine. If either antimony or tin were present they would remain in the original flask.—*Berichte*, vol. xxxiv., p. 33.

Action of Zinc Powder on Bromide of Trimethylene.—A. Volkof and B. Menschoutkine.—In a recent research the authors have shown that the action of zinc powder on bromide of trimethylene in alcoholic solution gives trimethylene mixed with propylene. If the alcohol is replaced by water, the reaction takes place at a temperature of about 70° , the disengagement of gas is rapid and regular, and the gas evolved is free from propylene, but even this gas is not pure trimethylene, it contains propane. It is impossible to describe the large number of experiments carried out to completely determine all the primary and secondary reactions which take place when zinc powder is made to react on bromide of trimethylene and its homologues under varying conditions; the conclusions to be drawn from the results only can be given:—1. The action of zinc powder and alcohol on bromide of trimethylene is analogous to that of these substances on the bromides of tetramethylene and pentamethylene; it produces a gaseous mixture formed of trimethylene, propylene, propane, and apparently a little hydrogen. 2. The presence of the propylene results from the formation,

by reason of the action of the zinc oxide contained in the zinc powder, of an ether, $CH_2Br-CH_2-CH_2-O-C_2H_5$, which, with zinc and alcohol, gives propylene. 3. The propane results from the action of the zinc powder on the bromide of propyl produced by the incomplete reduction of the bromide of trimethylene. 4. The action of bromine on the gas obtained in the reaction of the zinc powder on the alcoholic solution of bromide of trimethylene gives the following products:—Bromides of propyl and of isopropyl coming from the propane, and being almost entirely transformed by the bromine into bromide of propyl, bromides of propylene, and of trimethylene, resulting from the propylene and from the trimethylene. 5. The speeds of the reactions of bromine with propane, propylene, and trimethylene are very different; it is for this reason that the whole of the propylene cannot be removed by means of bromine, but we cannot separate the trimethylene and the propane by this means; by the action of bromine on this mixture we obtain bromides of propylene and of trimethylene; the amount of the former is so slight as to escape notice. It may be added that up to the present pure trimethylene has never been obtained; with zinc and alcohol, a mixture of trimethylene, propylene, and propane is obtained; with zinc and water, trimethylene and propane; and with sodium, trimethylene and propane.—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 118.

MEETINGS FOR THE WEEK.

TU. DAY, 25th.—Society of Arts, 4.30. "The Sphere of State Activity in Australia," by the Hon. Sir John Alexander Cockburn, K.C.M.G.

ANALYST AND ASSAYER (31).—Seven years' Colonial experience. Could take charge of Assay department. Unexceptional references. Interview anywhere desired.—Address, A. A. CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Applications are invited up to May 1st for the Position of ASSISTANT CHEMIST in an AUSTRALIAN MANUFACTURING INDUSTRY. Salary £600 per annum. Candidates must have received a thorough Scientific training at a University or Institution of University standing, and be, preferably, under twenty-six years of age.—Further details can be obtained by writing to Messrs. Parbury, Henty, & Co., of No. 20, Eastcheap, London, to whom applications are to be addressed.

CHEMIST (Tech. School Bergen, Norway; Tech. High Schools, Hanover, Berlin), desires Employment in Inorganic Laboratory (Analytical) Norwegian; thorough knowledge of English and German.—Address, P. Q., 54, Colebrooke Row, N.

WANTED.—A lot of odd Parts and Volumes of "Chemical News," "Journ. Chem. Soc.," "Analyst," "Sugar Cane," "Journ. Soc. Chem. Ind.," "Journ. Soc. Arts," and others.—Offers to "L. I., Burnett, Ashton, Preston.

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THE CHEMICAL NEWS.

Vol. LXXXV., No. 2209.

THE DENSITY AND COEFFICIENT OF CUBICAL EXPANSION OF ICE.*

By J. H. VINCENT, D.Sc., B.A., St. John's College, Cambridge.

AFTER an account of the methods employed by previous experimenters in the subject, reference is made to the views of Nichols, according to which two distinct kinds of ice have been subjected to experiments. The density of artificial ice is about 0.916 gm. per c.c., while that of natural ice is more than one part in a thousand greater.

Two tables are given showing in the first all the results which have been published concerning the density and coefficient of cubical expansion of ice, and in the second the same results tabulated separately according to the variety of ice used. The mean result for the density of natural ice at freezing-point is 0.9176, while that of artificial ice is 0.9162 gm. per c.c. Only one estimation of the dilatation of natural ice is available. It is 0.000125 for the cubical coefficient per degree C. The mean of three available results for artificial ice is 0.000160.

It was thought desirable to use a method of experiment which would yield a result both for the density and for the coefficient of cubical expansion, and in order that the work should have any value it was necessary to employ some device other than any which had been used previously.

The method consisted in weighing a quantity of water in mercury. The water was weighed both as liquid at 0° C., and as solid at several temperatures below freezing-point. If we assume values for the density of water and mercury at 0° C., the density of ice at 0° C. can then be calculated, if we also assume that the densities of ice and mercury are linear functions of the temperature. The coefficient of cubical expansion of ice can also be calculated from these results, but it will depend on the law assumed for the contraction of mercury, and upon the accuracy of the thermometry.

Instead of using a sinker to keep the vessel containing the water or ice under the surface of the mercury, a modification of Joly's hydrostatic balance was employed (Joly, *Phil. Mag.*, September, 1888).

Ten values of the density of ice at different temperatures below 0° C. were obtained in this way. The specimens of water were four in number, and the temperatures ranged from -10.02° to -0.37° C. The whole of the weighings taken with the final form of apparatus are included in these determinations.

In one experiment the values obtained show unmistakably that the same specimen of water may assume different densities on freezing.

The ten values of the density are set out as functions of the temperature on a chart, and a graphical method is used to extrapolate for five values of the density of 0° C. These five values have weights assigned to them proportional to the number of separate determinations of the density from which they are derived. The numbers thus obtained and the weights to be assigned to them are set out in the table below.

Experiment.	Density at 0° C.	Weight assigned.
1	0.916335	3
2	0.915460	2
3	0.916180	2
4	{ 0.915540	1
	{ 0.916060	2

Weighted mean 0.9160

We thus obtain 0.9160 gm. per c.c. as the density of ice at 0° C.

Four values for the coefficient of cubical expansion can be obtained from these results. They are:—

Experiment.	Coefficient of cubical expansion.
1	0.000155
2	0.000152
3	0.000153
4	0.000148
Mean.. ..	0.000152

The results of this investigation are that Nichols's value for the density of artificial ice is confirmed, but that since the same specimen of water can freeze into specimens of ice having different density, the use of the Bunsen ice calorimeter in absolute determinations must be limited to an accuracy of probably one in a thousand.

The expenses of this research have been in part defrayed by a Government grant from the Royal Society, and in part by the Cavendish Laboratory.

I wish to thank Professor J. J. Thomson, F.R.S., for his kind encouragement, and my thanks are also due to Mr. E. H. Griffiths, F.R.S., through whom I was led to undertake the investigation.

ON CERTAIN CHEMICAL AND PHYSICAL PROPERTIES OF HÆMOGLOBIN.*

By ARTHUR GAMGEE, M.D., F.R.S., Professor Emeritus of Physiology in the Owens College.

THIS lecture consists of two parts, of which the first is bibliographical and critical, the second experimental.

PART I.—Bibliographical and Critical.

The author commences by stating that a peculiar interest—the parallel of that which in the plant organism belongs to chlorophyll—attaches to hæmoglobin, for, unlike any other chemical component of the animal body, in virtue of its special chemical and physical attributes, this remarkable substance may in the strictest sense be said to possess a definite and unique physiological function.

The author then discusses certain facts in reference to hæmoglobin and its products of decomposition which have a close bearing on his researches, or which possess special interest in the light of work which has been recently done. He does so under the following heads:—

(1). The question of the identity of hæmoglobin throughout the animal kingdom. (2). The nature of the albuminous body which is linked to the coloured iron-containing group in hæmoglobin—*Globin (Hæmato-Histon)*. Under this heading he discusses the general properties of the histons and their relation to the simplest of all the albuminous bodies, the *Protamines*. (3). The products of the decomposition of the iron-containing molecular group in hæmoglobin. Under this heading the author directs special attention to the researches of Schunck and Marchlewski, which have shown by the oxidation of phylloaonin, one of the decomposition products of chlorophyll, a substance, *PHYLOPORPHYRIN*, is obtained which is probably identical with hæmatoporphyrin. Under this, as also under the preceding head, the author discusses various questions in reference to the seat of the synthesis of hæmoglobin.

PART II.—Experimental.

(1). *Extension of Previous Observations on the Absorption of the Ultra-violet Rays of the Solar Spectrum by Hæmoglobin.*

The author refers briefly (illustrating his remarks by demonstrations) to his researches, previously published,

* Abstract of a Paper read before the Royal Society, Feb. 6, 1892.

* Abstract of the Croonian Lecture read before the Royal Society, March 13, 1902.

into the absorption of the extreme violet and ultra-violet rays of the solar spectrum by hæmoglobin, its compounds, and certain of its derivatives. The region of the solar spectrum which he formerly investigated was that comprised between the lines F and Q (4861—3280).

He now examines the question whether oxy-hæmoglobin presents definite absorption for light of shorter wavelengths. Soret, whose observations were not conducted with solutions of hæmoglobin, but merely with diluted blood, observing by the aid of his fluorescent eye-piece the cadmium spark spectrum, found that diluted blood, in addition to the absorption band in the extreme violet, exhibited two additional bands. One of these, coinciding with the 12th cadmium line (3247), he considered to be probably due to hæmoglobin; the other, coinciding with the 17th cadmium line (2743), he assumed to be caused by serum albumin, his observations having previously shown that all albuminous and albumenoid bodies, with the exception of gelatin, are characterised by an absorption band in the position of the 17th cadmium line.

Employing solutions of many times crystallised oxy-hæmoglobin of great purity and of varying concentration, and with the aid of the sparks of a powerful induction coil, the author has obtained a series of photographs of the cadmium spark spectrum with and without the interposition of the solutions. The examination of these photographs shows that solutions of oxy-hæmoglobin which are sufficiently transparent to allow the ultra violet spectrum of cadmium to be photographed, present no absorption bands corresponding either to the 14th or the 17th cadmium lines. The absorption band observed by Soret in correspondence with line 14 is therefore not due to the blood colouring matter, but to some other organic constituent present in the blood.

(2). *Behaviour of Oxy-hæmoglobin and CO-hæmoglobin in the Magnetic Field. The Intense Ferro-magnetic Properties of Hæmatin and Hæmin.*

Having referred to his researches communicated to the Royal Society, in June, 1901, and illustrated the main facts by actual demonstrations, the author discusses (1) observations on the influence of temperature on the behaviour of oxy-hæmoglobin in the magnetic field; (2) observations on the ferro-magnetism of the ferro-albuminates.

(3). *The Specific Conductivity of Solutions of Oxy-hæmoglobin.*

The author next examines the question of the specific conductivity of solutions of pure oxy-hæmoglobin.

In this research he has worked exclusively with the hæmoglobin of the horse, and, following substantially the method of preparation which in Zimoffsky's well-known investigation yielded the purest product, he succeeded in obtaining crystallised oxy-hæmoglobin of remarkable purity, the ash of which consisted solely of oxide of iron with an indeterminate trace of P_2O_5 , and contained no trace of chlorine. He employed oxy hæmoglobin three times re-crystallised, and in addition to the thorough washing by decantation with 20 per cent alcohol after each successive crystallisation, he treated the ultimate product many successive times with large quantities of pure distilled water having a conductivity which never exceeded $10^{-6} \times 2.5$, the washed hæmoglobin being separated by the aid of the centrifuge. The solutions which formed the subject of investigation were made by dissolving the mass of moist hæmoglobin crystals in pure distilled water of $35^\circ C$, and cooling the solution thus obtained as rapidly as possible.

In his determination of specific conductivities, the author employed the method of Kohlrausch. The bridge was Kohlrausch's metre bridge, of which the platinum-iridium wire was 3 m. in length. This bridge is furnished with resistances of 1, 10, 100, and 1000 ohms, the precision of which had been kindly determined some years ago for the author by Dr. Glazebrook, F.R.S. The resistance

vessels employed were those known after the name of Arrhenius, and the temperature was kept constant by immersing them in one of Ostwald's thermostats furnished with a windmill stirrer.

After a laborious investigation on this branch of the subject, the author has arrived at the following conclusions:—

(1). Although solutions of oxy-hæmoglobin possess a low conductivity, this is very much higher than has been found in the previous observations of Stewart, all of which were made at $5^\circ C$.

(2). The conductivity of solutions of oxy-hæmoglobin increases rapidly with increase of temperature, and undergoes remarkable and permanent changes when the solution is kept for even short periods at any temperature above $0^\circ C$.

These results explain the impossibility of obtaining data which can be considered reliable concerning the absolute specific resistance of solutions of oxy-hæmoglobin.

The following numbers expressed in reciprocal ohms represent the mean of the author's results on the specific conductivity of solutions of oxy-hæmoglobin:—

T.		1. Contains 3.07 per cent of O ₂ Hb (or 1 grm.-mol. in 54290 grms.).	2. Contains 2.235 per cent of O ₂ Hb (or 1 grm.-mol. in 74580 grms.).
		Conductivity.	Conductivity.
0°		$10^{-5} \times 2.626$	$10^{-5} \times 2.23$
18°		$10^{-5} \times 4.432$	$10^{-5} \times 3.25$
25°		$10^{-5} \times 5.19$	$10^{-5} \times 4.27$
39°		—	$10^{-5} \times 7.47$

(4). *The Results of the Electrolysis of Oxy-hæmoglobin.*

1. Continuing the researches contained in his first communication to the Royal Society on this subject, the author finds that when pure solutions of oxy-hæmoglobin are subjected to electrolysis, there occurs a separation of oxy-hæmoglobin in a colloidal but perfectly soluble form. He has worked with currents of from 12 to 24 volts, and the intensity of the electrolysis current measured by a milliampère-meter placed in the circuit has varied in different experiments between 0.1 and 3.0 milliampères.

2. By employing an electrolytic cell in which the anode is separated from the kathode by an animal membrane (sheep's intestine or pig's bladder), it is seen that the first action of the current is to cause a separation of colloidal hæmoglobin in the anode cell. This colloidal hæmoglobin falls as a beautiful red cloud, leaving a perfectly colourless, supernatant liquid. On stirring it instantly dissolves.

3. The further action of the current is to cause a rapid and entire transfer of the colloidal hæmoglobin from the anode to the kathode cell. With an electrolytic cell, of which each compartment had a width of 5 m.m. and contained 2.5 c.c. of a 1 per cent solution of O_2Hb , complete precipitation and transfer occurs within sixty minutes.

4. On reversing the direction of the current by means of a commutator, the hæmoglobin returns again in the direction of the positive current into the original cell from which it started.

5. The author adduces evidence which proves that the precipitated colloidal, but yet perfectly soluble, hæmoglobin represents the undecomposed molecule of the blood colouring matter.

6. The probable nature of the process which occurs under the influence of the current is discussed, as well as the character of the process which leads to the transfer of the hæmoglobin in the direction of the positive current. This process the author considers to be of the same nature as the phenomena studied by Quincke under the name of electro-endosmose.

7. The author directs special attention to the importance of the facts which he has elicited in reference to the colloidal yet soluble form of oxy-hæmoglobin. He points out that all which has been said with regard to oxy-hæmoglobin applies to CO-hæmoglobin.

A typical colloid in the sense of its absolute indiffusi-

bility through animal membranes and parchment paper, oxy-hæmoglobin differs, however, from most colloids in the facility with which it crystallises. Hitherto we have known it in its crystalline condition and in solution in water. Now in its third or colloidal form the analogy with such a colloid as silicic acid is rendered complete.

The discovery of this form of hæmoglobin enables us to form a conception of the state in which the blood colouring matter is probably contained in the blood corpuscles. We have known that the amount of hæmoglobin contained in the corpuscles is so large that in most animals at least the whole of the water of the blood would not be sufficient to dissolve it. It was perfectly obvious, therefore, that it did not exist in the corpuscles in a state of solution, and the opinion has generally been held that these contained some unknown compound of oxy-hæmoglobin with a constituent of the stroma. It seems highly probable that in the red blood corpuscle hæmoglobin may be merely present in its colloidal form.

Finally, the author points out that the remarkable facility with which the new colloidal form of hæmoglobin traverses such permeable membranes as the animal membranes and even parchment paper, when its solutions are subjected to electrolysis, suggests to physiologists the possibility that certain of the phenomena of absorption in the animal body may be closely connected with electro-motive changes in the tissues concerned.

EXPLOSION BY HEAT, AND THE DISRUPTION OF BODIES INDEPENDENTLY OF THEIR CHEMICAL COMPOSITION.

By Dr. T. L. PHIPSON.

SHORTLY after the publication of my little work, "Meteors, Aërolites, and Falling Stars," which appeared in 1867, I made some experiments which led me to discover the cause of the explosion of meteorites when they pass into our atmosphere; and in 1869 I published a short note in the *Comptes Rendus* of the Paris Academy, "*Sur l'explosion et la chute des Météores*," in which I showed that when the surface of any body is suddenly raised to an intense degree of temperature, its interior being excessively cold, an explosion invariably occurs.

I alluded again to this in my recent work, "Researches on the Earth's Atmosphere," p. 67 (London: Griffin and Co., 1901), where I have written:—"The cause of the explosion of a meteor in the atmosphere is due to the sudden rise of temperature on the surface, which is thereby fused, whilst the interior is most intensely cold. . . . It has been estimated that if the speed of a meteor is only slackened by $\frac{1}{1000}$ th during its passage through the air, its temperature is raised on the surface to a much higher degree than that at which iron burns; and I have proved by actual experiment that the sudden heating of the surface of a body intensely cold in its interior, as a meteor coming from cosmic space must be, is quite sufficient to explain the explosion and rupture of the aërolite."

The disastrous explosion of chlorate of potash which occurred not long ago at St. Helens, has given rise to much discussion, and this month to a paper by Professor Dupré, read to the Society of Chemical Industry, in which he shows that beads of chlorate of potash exposed suddenly to a very intense heat will explode even when no reductive gas is present; and in the discussion which followed the reading of that paper, it was shown that M. Berthelot had already arrived at the same opinion shortly before. But I made a similar experiment in 1869, and arrived at this opinion thirty-three years before either Prof. Dupré or M. Berthelot.

My first experiment on this subject was a very simple one; I found that a substance which, when heated gradually, simply ignites, without any explosion whatever,

when suddenly exposed to the hottest part of a furnace at a white heat, invariably explodes.

I therefore consider myself justified in laying claim to the discovery of this phenomenon until any chemist can prove that he made the experiment I made previous to the year 1869.

It is evident that my little note in the *Comptes Rendus* for that year clearly pointed out that there is a hitherto unrecognised property in what we call *heat* or *caloric*, which causes in certain circumstances the explosion of bodies quite independently of their chemical composition.

Probably the same molecular force which, when acting slowly, produces what we call *dilatation* when acting in the above-mentioned circumstances, produces what is termed *explosion*. It is a subject which requires much further investigation, and may possibly lead to some modifications of the present theory; but, personally, I am no longer able to carry on such investigations.

Casa Mia, Putney, March 22, 1902.

THE ANALYSIS OF TIN ORES.

By J. A. MULLER.

THE different recognised methods for the estimation of tin do not, as a rule, give entire satisfaction, in so far as the exactness of the results obtained is concerned. The reduction of cassiterite, digested in aqua regia, by fusing with cyanide and weighing the metallic mass obtained after washing, drying, and fusion under a layer of stearic acid, only gives good results when the ore is approximately pure. But in the presence of inert bodies, such as quartz, the reduction of the powdered ore gives a very divided metallic residue, which cannot afterwards be collected into one button or ingot when melted under stearic acid.

The fusion of the ore with a mixture of carbonate of potash and sulphur gives a similar result. The attack is only complete with the pure binoxide; but, in the opposite case, the residue must be submitted to three or four successive treatments for the whole, or nearly so, to be extracted in the form of a sulpho-salt soluble in water.

To estimate the tin in cassiterite, W. Hampe (*Chem. Zeit.*, 1887, p. 19) weighs the pulverised ore in a porcelain boat and reduces it by heating for two hours in a current of dry hydrogen; after which he dissolves the tin formed in hydrochloric acid and estimates it in the usual manner.

It is clear that if the ore only contains binoxide of tin as the substance reducible by hydrogen, the difference in the weight of the boat before and after the reduction will enable us, if the reduction is complete, to immediately calculate the weight of tin contained in the substance under examination; and, further, this method has the advantage of being very rapid, for it is quite possible to effect a large number of reductions in the same tube at the same time.

I have endeavoured to decide what was the necessary and sufficient time for the reduction of binoxide of tin, by heating to a moderate red heat, for different times, known weights of pulverised cassiterite, either mixed or not with quartz, in a current of pure dry hydrogen, taking good care to regulate the flow of the latter so as always to have a large excess of the reducing gas.

By using 0.9981 grm. of cassiterite, previously digested in aqua regia, and containing 97.47 per cent of SnO_2 and 2.31 per cent of quartz, I found the loss of weight to be 0.2007 grm. after heating for two hours in hydrogen, and 0.2062 grm. after three hours; now theory gives 0.2068 grm. for the total reduction. With a mixture of 0.5334 grm. of cassiterite and 0.3282 grm. of quartz, the loss of weight was 0.1050 grm. after two hours, and 0.1102 grm. after three hours and a half; theory gives 0.1103 grm.

The preceding experiments show that it requires at least three hours to effect the total reduction of the stannic oxide.

The following experiments—of which the first two were made with the cassiterite previously employed, and the three last with a cassiterite containing 99.08 SnO₂, 1.10 SiO₂, 0.10 CuO, and traces of oxide of iron and zinc—show that three hours is sufficient in all cases:—

Mixture.		Loss of weight.		Calculated loss of weight.	Tin, per cent.	
Cassiterite.	Quartz.	After 3 hours.	After 4½ hours.		Found.	Calculated.
Grm.	Grm.	Grm.	Grm.	Grm.		
0.8118	0.2108	0.1690	0.1689	0.1682	61.20	60.92
0.4517	0.6167	0.0941	0.0940	0.0936	32.62	32.45
0.2354	0.7932	0.0490	—	0.0496	17.64	17.85
0.9757	—	0.2054	—	0.2055	77.96	78.01
1.5363	—	0.3242	—	0.3236	78.14	78.01

Thus, whether the binoxide of tin is mixed or not with inert bodies, the loss of weight in hydrogen enables us to estimate with a pretty fair approximation the percentage of tin in the substance analysed.

According to "Würtlz's Dictionary," the different minerals which are likely to be met with in the deposits of cassiterite are quartz, mica, topaz, fluor spar, apatite, blende, galena, mispickel, molybdenite, and wolfram.

Quartz, muscovite, and topaz do not undergo any change of weight when heated in hydrogen under the conditions of the above experiments. Of this I have made quite certain; they therefore do not interfere with the operation in any way. As to the other minerals, they can be removed by treating the powdered mixture successively, and several times, with hot aqua regia, hot water, a neutral solution of tartrate of ammonium (to eliminate a little sulphate of lead which might be present), and, finally, with ammonia and water to dissolve the molybdcid and tungstic anhydrides.

It is true that this separation offers practical difficulties, especially on account of the filtrations it is necessary to make *only* after complete deposition of the solid matters, as the pulverised bodies in suspension will pass through the best filter-papers.

Cassiterite loses practically nothing of its weight when heated with aqua regia. Thus, 1.9564 grms. of calcined cassiterite, previously submitted to the preceding series of treatments, were heated for three days at about 50° with 12 to 15 c.c. of aqua regia (2 volumes of fuming HCl and 1 volume of HNO₃ at 36° B.), the liquor being renewed every day. An insoluble residue was left which, after calcination, weighed 1.9558 grms.; in the solution I found 0.4 m.grm. of SnO₂ and 0.3 m.grm. of Fe₂O₃.

To make quite certain up to what point we could count on the exactness of the results obtained in the particularly inconvenient case of a mixture containing galena and wolfram, a mixture was made of the three following finely powdered minerals:—Cassiterite at 99.08 Sn, 0.5859 grm.; galena,* 0.4532 grm.; and wolfram,† 0.3993, which I submitted three separate times to the series of treatments already described. Finally, the residue, previously calcined at a red heat, was submitted to the action of hydrogen. The loss of weight was 0.1239 grm., which corresponds to 31.9 per cent of tin in the mixture, while there was actually 31.78 per cent; the agreement is thus very satisfactory.

After heating the digested mineral in hydrogen, the residue may be treated with fuming hydrochloric acid and the solution analysed by weighing the tin in the form of

* After treatment by aqua regia, &c., 1.671 grms. of this galena left a residue weighing 0.0586, which lost none of its weight at a red heat in hydrogen.

† A beautiful sample, of which the density was 7.13, and which gave the following analysis:—

WO ₃ sol. NH ₃	74.67 per cent
Insoluble part NH ₃	1.22 "
FeO	11.07 "
MnO	12.12 "
CaO	1.26 "

100.34

binoxide, after precipitation as sulphide, treating with sulphide of sodium, &c.; it is in this manner that the cassiterites used in this research were analysed.

I have endeavoured to apply the above-described method of estimating tin, applicable to cassiterite, to stannine, which is a sulphurised ore of tin.

For this purpose the pulverised stannine was calcined at a dull red heat in a muffle; then, after treating the residue with a little nitric acid, it was dried and re-calcined; then treated again with nitric acid, dried at 110°, and digested first with dilute nitric acid, then with aqua regia. The residue thus obtained should consist entirely of bin-oxide of tin, quartz, and silicates, which are not attacked by the above treatment. As a matter of fact, this residue always contains a small quantity of ferric oxide, which I have never succeeded in completely eliminating, even by repeated treatments with aqua regia. Thus, in one experiment, 1.4414 grms. of stannine gave a residue which weighed, after calcination at a red heat, 0.4865 grm., and of which 0.4837 grm. lost 0.1036 grm. in hydrogen; this corresponds to a proportion of tin equal to 26.77 per cent. Now, the examination of the different solutions resulting from the treatment of the calcined stannine, and the analysis of the residues after the action of the hydrogen and treatment with hydrochloric acid, has given me the following figures for the composition of this stannine, supposing all the metals were in the form of sulphides:—

	I.	II.	III.
SnS ₂	38.48	38.36	38.48
Cu ₂ S	33.72		
FeS	16.87		
ZnS	8.55		
Quartz	1.45		

99.07

This stannine therefore contained 24.94 per cent of tin, while the estimation quoted above gave 26.77 per cent.—*Bull. Soc. Chim.*, Series 3, xxv., No. 23.

MOUNT VERNON LOESS.

Loess occurs to a considerable depth on the hills in the vicinity of Mount Vernon, Iowa. On the somewhat elevated ridge on which Cornell College is located, the formation extends to a depth of 40 feet, diminishing from the summit. In general it overlies the Kansan and Paha drifts, but it is usually absent over the Iowan.

A brickyard is located in the Mount Vernon Loess from which a good quality of brick is obtained.

The specimen chosen for analysis was taken from the brickyard, 8 feet below the surface of the earth.

The analysis was made by Frank Hann, in the Chemical Laboratory of Cornell College, under the direction of Dr. N. Knight.

The following results were obtained:—

	Per cent.
SiO ₂	70.86
CO ₂	4.70
Fe ₂ O ₃	2.97
Al ₂ O ₃	8.91
MnO ₂	0.28
CaO	4.13
MgO	3.12
K ₂ O	1.18
Na ₂ O	1.69
TiO ₂	0.59
P ₂ O ₅	0.40
FeO	0.10
H ₂ O	1.10

99.98

By MM. LEIDIE' and QUENNESSEN.

The *platinum* forms a platinate of sodium, insoluble in water, but soluble in hot hydrochloric acid; it is thus found in the precipitate. This latter is treated with hot hydrochloric acid to dissolve it. The solution is eva-

A. A solution.
B. A precipitate.

A. The solution is coloured.

B. The solution is colourless. It is thrown away, and the precipitate treated with HCl. The filtered liquor is treated with NO_2Na , then with CO_3Na_2 . Filter.

The filtered solution is treated with excess of HCl and evaporated nearly to dryness. Take up with water.

The solution is of a light *yellow* colour. With NH_4Cl it gives a yellow precipitate insoluble in excess of NH_4Cl Platinum.

<i>Blue colour.</i>	Neutralise with HCl.	Evaporate in the presence of HCl with HNO ₃ and KCl.	Iridium.
Black crystals,	insoluble in KCl		

More or less deep *yellow* colour. Submitted to a current of chlorine while hot.

A substance is volatile which gives a black precipitate with NH_4S .

The distilled solution gives an insoluble violet osmiate with hot KNO_3 . No brown colouration with HCl Osmium.

Nothing volatilised. No black precipitate with NH_4S in the distilled liquor.	Neutralise with HCl ; evaporate in the presence of HCl with HNO_3 and KCl . Red crystals insoluble in HCl .	Palladium.
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porated down to drive off the greater part of the acid, then treated first with nitrite of sodium and then with carbonate of sodium. In this manner the platinum, as well as the nickel resulting from the attack of the crucible, are both transformed into double nitrites; now this salt of nickel is precipitated by carbonate of sodium, while the platinum salt is not; thus on filtration we have a solution containing platinum free from nickel.*

The double nitrite of platinum and sodium is transformed into chloroplatinate of sodium by evaporating down, after the addition of hydrochloric acid in excess. The residue, taken up with water and treated with chloride of ammonium, gives chloroplatinate of ammonium of a yellow colour, and insoluble in an excess of the reagent.

The rhodium is transformed into a binoxide, insoluble in water, but soluble in hot hydrochloric acid. The precipitate containing it is treated with hot hydrochloric acid; after filtration the solution is evaporated to drive off the acid, then treated with nitrite of sodium and carbonate of soda, as in the case of platinum; the nitrite of nickel is precipitated by the carbonate of soda, while that of rhodium is not. The solution of this latter, decomposed by hot hydrochloric acid, gives the double sesquichloride, $\text{Rh}_2\text{Cl}_6\text{NaCl}$, of which the solution is red, and does not give any precipitate with chloride of ammonium.

The results are summarised in the accompanying table, which will serve as a guide for a qualitative analysis.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1902.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford again shows a serious deficit; the actual amount of rain measured was only 0.95 inch,

the average fall is 1.80 inches; this makes a deficit of 0.85 inch, and, added to the deficit recorded in January, makes a total shortage of 2.27 inches, or 58.5 per cent on the thirty-five years' average.

Our bacteriological examinations of 485 samples have given the results recorded in the following table; we have also examined 36 other samples, from special standpipes, wells, &c., making a total of 521 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	197
New River, filtered (mean of 117 samples) ..	9
Thames, unfiltered (mean of 23 samples) ..	3329
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 264 samples) ..	27
Ditto ditto highest	205
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	233
River Lea, from the East London Company's clear-water wells (mean of 33 samples) ..	8

Of the 414 samples of impounded and filtered water supplied to London and examined bacteriologically during the past month, 13 samples, or 3.1 per cent, were sterile. Only two samples contained more than 150 microbes, while only nine samples, or 2.1 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the nine excess samples was 143, against a corresponding mean of 143 in thirty excess samples during January.

It will be seen that, although there has been a smaller number of sterile samples during this month, there has been a still greater decrease in the number of samples containing over 100 microbes, with the satisfactory result that the average has been reduced. This is not to be wondered at, considering that the supply of the River Thames has been drawn largely from the storage in the great chalk deposits, consequent on the very small rainfall during the month in the valley of the Thames.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

CN PYRITE AND MARCASITE.*

By H. N. STOKES.

(Concluded from p. 136).

XII. CONSTITUTION OF PYRITE AND MARCASITE; ACTION OF CUPRIC SALTS (continued).

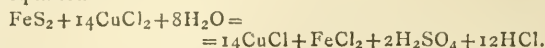
Experiment with Cupric Chloride and Pyrite.

Experiment 6.—0.2545 grm. pyrite was heated with 50 c.m.* of a pure cupric chloride solution containing as much copper as the sulphate used in the foregoing experiments; the tube being filled with the usual precautions to prevent oxidation. The tube was heated five hours at 200°, and on cooling was found to contain undecomposed mineral and an abundant crystallisation of cuprous chloride. The filtered solution gave—

0.0667 grm. iron = 0.1429 grm. pyrite.

0.5540 grm. BaSO_4 = 0.1427 grm. pyrite.

It appears, therefore, that as far as it was decomposed the pyrite was completely oxidised to ferrous salt and sulphuric acid, with a corresponding reduction of the copper from the cupric to the cuprous state, according to the equation—



I have further obtained an abundance of sulphuric acid by

* All metals, without exception, are attacked by binoxide of sodium under these conditions. We have chosen nickel (chemical dishes, &c., made of this metal are easily obtained), firstly, because its oxide is insoluble in water, which fact enables us to separate it from osmium, ruthenium, palladium, and iridium, and also because its double nitrite of sodium is precipitable by the alkaline carbonates, while the double nitrites of platinum and rhodium are not; this enables us to separate the platinum and rhodium. It is one of the general properties of the double nitrites of the metals platinum and sodium not to be precipitated by the alkaline carbonates. This is the basis of the general method devised by M. Leidié for the extraction and separation of the metals of the platinum group. See E. Leidié, *Comptes Rendus*, vol. cxxxi, p. 838; *Bull. Soc. Chim.*, [3], vol. xxv, p. 9; *Journ. Pharm. et Chim.*, [6], vol., xiii, p. 18.

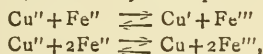
* From the Bulletin of the U.S. Geological Survey, No. 186.

oxidising precipitated copper sulphide with cupric chloride solution at 100°, air being rigorously excluded. Doubtless in the above experiments with pyrite and marcasite and copper sulphate an analogous oxidation occurs, being obscured by other reactions. Chalcocite, however, is not perceptibly attacked by 10 per cent copper sulphate solution after fourteen hours' heating at 200°.

Experiment with Ferrous and Cupric Sulphates.

Experiment 7.—A mixture of equal volumes of 10 per cent solutions of crystallised copper sulphate and crystallised ferrous sulphate (carefully freed from ferric salt by reduction with hydrogen sulphide) was heated, under absolute exclusion of air, for three hours at 200°. A considerable red precipitate was obtained, which consisted of a mixture of ferric oxide or basic sulphate with cuprous oxide and apparently metallic copper. The reduction of cupric by ferrous salts in neutral or acid solution is frequently referred to in the literature, but, so far as I can ascertain, without experimental basis.

Theory of the Reaction.—The explanation of the result is probably the following:—In the mixture we have equilibrium between the cupric, cuprous, ferrous, and ferric ions and copper, as represented by the equations—



in which but traces of Cu, Cu', and Fe''' exist. (The slight solubility of cuprous compounds shows that not more than traces can be present). On heating, the trace of ferric salt is precipitated in the basic form, the equilibrium is disturbed, and the reaction continues to proceed from left to right, accompanied by formation of Cu' and Fe''' (and possibly Cu) and their precipitation as insoluble products, until the accumulated acid is in equilibrium with both of these and further precipitation cannot occur. The process is further complicated by a partial precipitation of copper as basic salt when the sulphate is used. A mixture of cupric and ferrous salts gives a strong reaction for ferric iron with sulphocyanate. This does not imply an appreciable oxidation of the ferrous iron in the mixture itself, but a shifting of the equilibrium to the right in the above equation through the formation of the slightly dissociated ferric sulphocyanate. It is doubtless to the reduction of the cupric sulphate by sulphur and by ferrous sulphate that the formation of chalcocite from pyrite is to be ascribed.

General Conclusions from the Experiments.

The conclusions which may be drawn from the above experimental data are:—

1. At 200° copper sulphate decomposes marcasite more rapidly than pyrite.

2. Both ferrous and ferric salts are formed in both cases, the former being found wholly in the solution, the latter wholly in the precipitate. There is no marked difference in the relative amounts of these in either case. The precipitate also contains, besides cuprous sulphide, cuprous oxide and perhaps metallic copper.

3. The formation of ferric salt is to be ascribed, in part at least, to the reaction of the ferrous salt upon the cupric salt (Experiment 7), while some oxidation of sulphur to sulphuric acid occurs (Experiment 6). Any ferric salt which may fail to be precipitated will be reduced by the sulphides.

4. The relative amounts of ferrous and ferric salts depend simply upon the establishment of equilibrium between the solution and the products of decomposition of the pyrite or marcasite, and not upon any fundamental chemical difference in the two minerals, and consequently the hypothesis of Brown is devoid of valid experimental basis.

It would seem that no method can be depended upon to give us an insight into the state of combination or valency of either iron or copper in their sulphides which does not take due account of the conditions of equilibrium

between the reagents and the decomposition products. This applies not only to other experiments of Brown quoted in his paper, but to the attempt of Starke, Shock, and Smith (*Journ. Am. Chem. Soc.*, 1897, vol. xix., p. 948) to prove the divalent condition of iron in arsenopyrite, and of Morgan and Smith (*Journ. Am. Chem. Soc.*, 1901, vol. xxiii., p. 107) to establish the same for chalcopyrite. That the product of heating chalcopyrite in dry hydrochloric gas consists of a mixture of cupric chloride and ferrous chloride is inconclusive on the question as to whether chalcopyrite has a constitution represented by (Cu''Fe'')S₂ or (Cu'Fe''')S₂ until the condition of the system $\text{CuCl} + \text{FeCl}_3 \rightleftharpoons \text{CuCl}_2 + \text{FeCl}_2$ in equilibrium is known, in the absence of water and presence of hydrochloric acid gas. That nearly all the iron was obtained in the ferrous state in some of the experiments with copper sulphate made by Brown and others I can explain only on the assumption that enough acid was originally present or eventually formed to enable any basic salt to act on and be reduced by the residual sulphides and cuprous oxide. In fact, hot dilute sulphuric acid slowly dissolves the mixture of cuprous oxide and basic ferric salt obtained in my experiments, giving a strongly reducing solution.

XIII. OXIDATION OF PYRITE AND MARCASITE BY POTASSIUM PERMANGANATE.

(For previous experiments on the action of permanganate on pyrite and marcasite see A. P. Brown (*Proc. Am. Phil. Soc.*, 1894, vol., xxxiii.; and *CHEMICAL NEWS*, 1895, vol. lxxi., pp. 131, 155, 171). The experiments of Brown show that, with an excess of permanganate, the total sulphur oxidised in a given time is greater in the case of marcasite than of pyrite, but they do not establish any relation between the amount of sulphur oxidised and the quantity of mineral decomposed).

A few experiments were made to determine the percentage of sulphur oxidised in pyrite and marcasite at ordinary temperature by acidified permanganate, the mineral being always in excess.

An excess of the powdered mineral, freed from oxidation products, was shaken in a stoppered cylinder with a constant amount of dilute sulphuric acid and 100 c.m.³ KMnO₄, added in quantities of 5 c.m.³ at a time, the shaking being continued after each addition until the colour had disappeared, which required but a few minutes. The filtered solution was then reduced and the iron titrated by the same permanganate solution.

The proportions required are—

For complete oxidation to Fe₂(SO₄)₃
and sulphuric acid 5FeS₂ + 15KMnO₄

For oxidation of the iron alone to
Fe₂(SO₄)₃ 5FeS₂ + 3KMnO₄

For oxidation of the sulphur 12KMnO₄

Let—

a = volume of permanganate used in oxidation of FeS₂,

and—

b = volume of permanganate required to re-oxidise FeO to Fe₂O₃;

then—

$3b$ = volume of permanganate used in oxidising Fe in FeS₂ to Fe₂O₃,

and—

$a - 3b$ = volume of permanganate used in oxidising S in FeS₂ to SO₃;

also—

$12b$ = volume of permanganate required to oxidise all the sulphur in the mineral decomposed;

whence—

$$\text{Percentage of sulphur oxidised} = \frac{100(a - 3b)}{12b} = \frac{8.333a}{b} - 25.$$

Where 190 c.m.³ of permanganate are used,—

$$\rho = \frac{833 \cdot 3}{b} - 25.$$

The values of ρ obtained were—

	1.	2.
Pyrite	94 ⁰	90 ⁷
Marcasite.. .. .	84 ⁶	86 ⁷

The duplicate results are therefore not sufficiently concordant, nor is the difference between pyrite and marcasite great enough, to give the method more than a confirmatory value. The difference here, as in the case of oxidation by the ferric sulphate method, is due to the greater ease with which marcasite is attacked, but the relative oxidation rate of the sulphur is clearly much greater. The difference might possibly be greater at 100°, but here the experiments failed because of the strong tendency of the permanganate to deposit peroxide, even in the presence of much sulphuric acid.

XIV. SUMMARY OF RESULTS.

The chief results of this investigation may be thus summarised:—

1. When pyrite or marcasite is boiled with an excess of a solution of ferric salt to complete reduction of the latter, the ratio of sulphur oxidised to mineral decomposed is perfectly definite and characteristic of each mineral, provided certain standard and easily controllable conditions are observed. Under these conditions the percentage of sulphur oxidised in pyrite is about 60·4 per cent and in marcasite about 18 per cent of the total sulphur. These figures are the characteristic *oxidation coefficients*.

2. The oxidation of pyrite or marcasite to ferrous salt, sulphuric acid, and free sulphur cannot be expressed by any single equation, but takes place according to two or more, the relation between which varies with the special conditions.

3. An empirical curve for the oxidation coefficients of mixtures of pyrite and marcasite is constructed by aid of which the composition of naturally occurring mixtures may be quantitatively determined.

4. The influence of various impurities on the results is described.

5. Various concretions and other specimens are examined, and it is shown that in many cases much uncertainty exists in distinguishing pyrite and marcasite by the usual methods.

6. There is no well-established evidence of the existence of true paramorphs of pyrite after marcasite or of marcasite after pyrite.

7. The hypothesis that most natural specimens, even when well-crystallised, are intimate mixtures of the two is without foundation.

8. Specimens crystallising in the regular system are true pyrite, while those forming rhombic crystals are true marcasite. When the two are mingled or intergrown, it is generally possible to distinguish each by the colour after cleaning with acid—a rule to which there are a few exceptions.

9. The density does not afford a trustworthy means of determining one mineral in the presence of the other.

10. Chalcopyrite may be sharply distinguished from chalcocite or bornite in pyrite carrying 3 per cent copper or less. A method is given for detecting small amounts of chalcopyrite in pyrite and marcasite, or the reverse, or in rocks.

11. There is no evidence as to the state of combination or valency of iron in pyrite and marcasite, or that these differ in the two minerals. Experiments which have been regarded as proving the existence of such differences are inconclusive.

12. The principle of the oxidation method, with appropriate modifications, is probably capable of wider application in distinguishing dimorphous minerals, in determining whether a given complex mineral is a mixture or com-

pound of its simpler constituents, and in determining the nature of small amounts of impurities.

13. The action of acid permanganate on pyrite and marcasite is analogous to that of ferric salts, the percentage of sulphur oxidised in pyrite being higher than in marcasite.

My thanks are due to Dr. A. A. Julien, whose valuable assistance has been noted above, and to Professors Van Hise, Emerson, Merrill, and Penfield, and Messrs. Tassin, Emmons, Ransome, Weed, and Lindgren, who have generously supplied most of the material upon which the foregoing investigation is based.

NOTICES OF BOOKS.

The Elements of Physical Chemistry. By J. LIVINGSTON R. MORGAN. Second Edition, Revised and Enlarged. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1902. Pp. x-352. 12mo.

SINCE publishing the first edition of this book noticed in CHEMICAL NEWS, vol. lxxix., p. 129 (March 17, 1899), the author has done three things to improve it; he has brought the subject-matter itself up to date, he has made the relations clearer than before, wherever possible, and he has endeavoured to make the volume more useful to those studying the subject without an instructor. A few things found to be superfluous have been omitted, and a number of new relations have been added; also 150 problems.

This comprehensive outline of subjects that have been treated in independent volumes is so arranged as to economise the time that the average student can spare for this branch of chemistry; at the same time those desirous of extending the study of any special portion can do so with the aid of the references given. The calculus is introduced in devising some of the laws, but most of the work requires no special training in the higher mathematics.

Those wishing to pursue the study of physical chemistry along the lines of modern research, especially with reference to solution, thermochemistry, the laws affecting chemical change, and electrochemistry, will find this useful manual generally up to date and reliable. The subject of phases is but briefly treated, and reference is made to the special treatise by Wilder Bancroft, "The Phase Rule."

The author lays no claim to originality, but acknowledges his indebtedness to Ostwald, to Le Blanc, and to Nernst. The book is well printed, and has an index. H.C.B.

Manual of Alcoholic Fermentation and the Allied Industries. By C. G. MATTHEWS, F.I.C., F.C.S. London: Edward Arnold.

THIS book contains, amongst others, chapters on the life-history of the saccharomycetes, chemical science and the carbohydrates, the preparation of wine, and the brewing process. From these titles it will be seen that its scope is fairly large, and that it is intended to appeal to a wide circle of readers; probably it would have been wiser to have restricted its aim.

At the very outset exception must be taken to the definition of fermentation, and the review of the present state of our knowledge of the theory of fermentation is not entirely up-to-date. The full significance of Buchner's work on the isolation of zymase, and the essential difference between regarding fermentation as a vital metabolic process of the yeast, and assuming the presence of an enzyme produced by the yeast cells, seem to have been hardly realised by the author. Much of the chapter on chemical science either requires fuller treatment, or had better have been omitted altogether; both the student and technologist might well be expected either to have

a previous knowledge of chemistry, if only of an elementary nature, or at least to be able to acquire it from other sources. Moreover, the accuracy is not always beyond dispute, nor the wording happy. For the practical man details of the brewing process would probably be insufficient, and no mention is made of the diseases of beer, though those of wine are briefly touched upon; the brewery plant, too, might well have been described in fuller detail. A word of praise must be given to the plates and illustrations, which are very clear and good.

Die Wissenschaftlichen Grundlagen der Analytischen Chemie. By W. OSTWALD. Leipzig: Wilhelm Engelmann. 1901.

The aim of this book is expressly stated to be not the teaching of analytical chemistry as such, but the explanation of the theoretical groundwork underlying analysis; hence, with this object in view, few practical details are to be found in it, while no theoretical point is overlooked. The book is characterised by Dr. Ostwald's well-known thoroughness of treatment in regard to details, too often hurriedly passed over, or altogether neglected in elementary text-books, such as, for example, the theory of the washing of precipitates and of distillation. As we should expect from so staunch a champion of the ionisation theory, the subject is attacked from an ionic standpoint. Beginning with purely theoretical considerations, the first part deals with the recognition and separation of substances in general, both by physical and chemical means, and ends with a short account of the theory of methods of quantitative separation. Dr. Ostwald's style makes this part of the book particularly attractive reading. The second part contains, under the headings of the several elements, the theory of the application of general principles; methods of separation are not neglected, but no tables for detection and separation are given. In the appendix a few experiments illustrative of the text are briefly described, admittedly by no means sufficient in number; the amplification of these, however, may well be left to the choice and discretion of the teacher.

The book has well deserved its success, but we should have expected to see a third edition quite free from even trifling misprints, and an index would probably be appreciated by those who may have occasion to refer constantly to the book.

Ferments and their Actions. By CARL OPPENHEIMER, M.D., Ph.D. Translated from the German by C. AINSWORTH MITCHELL, B.A. (Oxon.), F.I.C. London: Charles Griffin and Co., Ltd. 1901.

THE translation of this thoroughly scholarly treatment of a wide and difficult subject deserves a good reception in England; the translator's work has been well done, and in some instances he has, with the author's sanction, introduced the results of investigations published since the appearance of the German edition; we could wish—though of course this is a minor point—that italics had been a little more sparingly used.

The word ferment is used in its widest sense, though putrefactive processes and the so-called butyric acid fermentation are omitted. An exceedingly cautious definition of a ferment provides a subject for masterly chapters on the conception of the nature of a ferment, and the chemical nature of ferments, in which various hypotheses are fairly discussed, even if ultimately dismissed as untenable. The ferments are classified under the headings hydrolytic and oxidising; for the present, lactic acid fermentation is included with the former, perhaps without very good reason. Every effort has been made to give the results of the most recent researches, a very essential point in such a work; so rapidly is our knowledge of physiological chemistry growing, however,

that every month sees a change in our views; for instance, the action of trypsin on pepsin, contrary to our author, has been recently shown to be not altogether negligible.

The whole is well indexed and arranged, and liberal acknowledgments are everywhere made, and references given to original papers, the author believing firmly in the necessity for reference to original publications for experimental details.

Water and its Purification; a Hand-book for the Use of Local Authorities, Sanitary Officers, and Others interested in Water Supply. By SAMUEL RIDEAL, D.Sc. (Lond.), F.I.C., &c. With numerous Illustrations and Tables. Second Edition. Revised and Extended. London: Crosby Lockwood and Son. 1902. Pp. 346.

PURE water, as the term is generally understood, is very different to really pure water from the chemical point of view. The best water for human use should contain a variety of substances held in solution, such as salts of lime, sodium, &c., as well as gases, such as carbonic acid and free oxygen, all of which help to make it palatable. There are, however, other substances which should always be kept out of water as far as possible when it is intended for dietetic purposes.

The main object of this book is to give some insight, to those interested in the subject of water supply, into the methods of research as to the quality of various waters, and the interpretation of the results obtained. Although it is impossible for any but a trained expert to interpret the results of analyses with accuracy, it often happens that a report might be made more easy of comprehension to an ordinary reader; at the same time it must be insisted upon, that the so-called rough and ready tests are so likely to be misleading as to be practically valueless.

The ordinary suspended impurities to be found in raw waters may be divided into three classes, viz., vegetable, animal, and mineral; practically all these can be removed by efficient filtration, and even germs of disease may be so few in number as not to be found in every sample; on the other hand, chemical products being dissolved will be found throughout. These products exist in great variety, and form a good index of the permanent character of the water.

Experience has shown that sand filtration is not only the best means for removing suspended matters on the large scale, but also, through the formation of the surface slime on the filter, for the oxidation of the organic matter dissolved in the water by the combined help of the microbes present and the oxygen held in solution. A sand filter does not attain its maximum efficiency until this slime has been formed. After a time, however, the growth increases to such an extent that the bed becomes clogged, and it becomes necessary to renew the whole of the surface layer.

It not infrequently happens that a water contains a considerable amount of lime and magnesia salts; it is known as hard water, and, besides not being so good for domestic use, it is very unfit for manufacturing purposes. It then becomes necessary to soften it; one of the best known methods for effecting this is Clarke's process; this and other methods are dealt with very fully in Chapter X.

The chapter on analysis and its results is of interest, but the subject is only lightly dealt with. The combustion process of Frankland and Armstrong is accorded only a few lines more than a page, and then only to point out a few possible sources of error. We must take exception to the author's remarks on this method of determining the organic carbon and nitrogen in water, as every one of these objections indicates either lack of knowledge or lack of skill in carrying out the process. We admit that the process is not simple, like the estimation of the organic matter in solution by means of permanganate of potash, but in the hands of a careful and well-trained chemist, trustworthy results can be obtained with remarkable

accuracy, and not only the amount but the character of the organic matter is also shown, whether of animal or of vegetable origin, which cannot be done with any degree of certainty by any other method.

The appendix deals with some recent epidemics connected with water supply, and suggestions for legislation in connection therewith. There are some useful tables giving typical examples of water analyses, the composition of boiler incrustations, the order of the rocks, and characteristics of waters derived from them, &c., while the index, which fills twenty-six columns, is exceptionally complete.

Property in Trade Marks. Being a Manual Written, without the Use of Legal Phraseology, on Trade Marks and their Protection. By BREWER and SON, Patents, Designs, and Trade Marks Agents. London: Taylor and Francis. 1902. Pp. 78.

THE ordinary works on the subject of trade marks are written in such highly technical language that, though they are of great value to specialists who have made a study of the subject, they are of little or no use to the manufacturer or trader who wishes to arrive at a clear understanding of the law relating to property in trade marks.

The object of this book is to enable the users and prospective users of trade marks to glean some knowledge of the intricate law governing this matter; and it is also suggested that patent agents and solicitors, who only occasionally have to deal with such matters, will find in it information which will be of service to them.

A trade mark must be a "distinctive" sign, and not merely a descriptive adjective or word, as no person has the right to appropriate to himself any word or sign which is the common property of the public.

The use of a trade mark is to afford a ready means by which the public may recognise any particular goods, and hence its value.

A trade mark must comply with one or more of five definition clauses which are fully explained, but there are also several restrictions to be specially noted. The Royal Arms cannot be registered, nor portraits of the King and Queen, or any member of the Royal Family; no word will be accepted in the possessive case, nor can letters of the alphabet or figures be registered.

In the official classification list, goods are divided into fifty classes for which a trade mark can be registered, and separate registrations are required for each class. Some of these classifications are rather quaint; for instance, Class 14, goods of precious metals (including aluminium, nickel, Britannia metal).

Besides those of Great Britain, this book deals with foreign and colonial trade marks, though only in a general way.

The book is clearly written and well printed, and indexed.

The Chemistry of Organic Colouring Matters ("Chimie des Matières Colorantes Organiques"). By R. NIETZKI, Professor at the University of Bâle. Translated into French from the Third German Edition, and Revised from the Fourth German Edition by C. VAUCHER, C. FAYRE, and A. GUYOT. Paris: G. Carré and C. Naud. 1901. Pp. 447.

THOUGH there are some excellent books in France dealing with colouring matters, especially those by M. Lefèvre and MM. Seyewetz and Sisley, they are all too bulky, and their study would require a large amount of time. The present volume has the double merit of being both concise and complete; it is not intended solely for the use of those who wish, later on, to make colouring matters their principal study, but also for the more numerous class who are daily engaged in their application.

Dyers, paper-makers, lacquer makers, and in fact all

those who have to do with the manufacture and dressing of skins, leather, feathers, waxes, &c., see the increasing necessity of no longer using products whose chemical nature is unknown to them; it is evident that this knowledge must be of great assistance, and will prevent many useless experiments.

The division of colouring matters into natural families was first inaugurated by M. Nietzki in the year 1886. The best proof of its excellence is that it has been adopted universally, both in literature and in teaching.

The book is divided into thirteen different sections or chapters, beginning with nitrated colouring matters, after which the author goes through all the other groups and families, such as the oxyquinones, the di- and tri-phenylmethanes, quinoneimide and its derivatives, aniline black, quinoleine and acridine, the oxyketones, xanthenes, flavones, and coumarines, &c., winding up with a chapter on colouring materials of unknown composition.

The index is exceedingly complete, and is divided into two parts, one alphabetical and the other bibliographical. There is also a small list of errata, none of which, however, is of great importance, being principally slight mistakes in spelling.

CORRESPONDENCE.

PETROLEUM LAMPS.

To the Editor of the Chemical News.

SIR,—I have just obtained a copy of Captain Thomson and Boverton Redwood's "Handbook of Petroleum," and find, on page 272, Appendix XI., suggestions for the care and use of petroleum lamps. As I have had considerable experience in shale oils here, I would like to add to them.

In all mineral oil lamps the oil continually creeps all over the reservoir, especially when the metal work is fastened on with plaster-of-Paris and size. This can be completely prevented by smearing the joint with glycerin, which can be easily done by dipping the forefinger in it and going once or twice round the joint inside the lamp. It is necessary to do this before oil is used; that is, when the lamp is new, as the glycerin will not penetrate if the plaster is saturated with oil, and conversely, the oil will not penetrate if it is saturated with glycerin. It is advantageous to lubricate all tap-plugs, washers, &c., with glycerin when they are brought in contact with mineral oil of any kind.

Under No. 14 it is said:—"Do not continue to burn the oil until it is completely exhausted. It is best to keep the lamp well filled." If this is done, the oil in glass reservoirs gradually becomes yellow, especially if exposed to light, and such oil encrusts the wick and burns badly. Lamps in churches are used seldom, and hence the oil is always in that condition. Lamps should be emptied occasionally, and the residues may be collected and burned off in one filling to a small bulk, the residue being thrown away.

Glass lamps when not in regular use should be kept in the dark.—I am, &c.,

W. A. DIXON.

97, Pitt Street, Sydney, February 17, 1902.

Researches on Calcium Silicide, CaSi_2 .—H. Moissan and W. Dilthey.—Lime, when kept in a state of fusion in presence of an excess of silicon, causes the formation of a compound of formula CaSi_2 , analogous to Vöhler's silicide. The action of this new silicide on water cannot be compared with the action of calcium carbide. Water is very slowly decomposed by this silicide, with evolution of hydrogen. Dilute hydrochloric acid attacks it much more rapidly; hydrogen is evolved, but no solid silicon hydride is produced.—*Comptes Rendus*, cxxxiv., No. 9.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 9, March 3, 1902.

New Synthesis of Methane.—Paul Sabatier and J. B. Senderens.—The authors compare the various syntheses of methane which have been effected up to the present, and add to these their own method of direct hydrogenation, by the action of gaseous hydrogen in presence of recently reduced nickel, either on carbon dioxide or on carbon monoxide.

Dilatation of Steel at High Temperatures.—Georges Charpy and Louis Grenet.—From a series of tables the authors have drawn up by means of direct measurement, it is seen that the dilatation of steel at low temperatures presents curious variations according to the amount of nickel present in the steel; but the coefficients of dilatation increase rapidly with the temperature so as to mask these variations.

Specific Heat and Atomic Mass of Vanadium.—C. Matignon and E. Monnet.—The authors (1) prove the existence of the crystalline compound AlVa ; (2) find certain interesting properties of ferro-vanadium; (3) determine the specific heat of the metal vanadium to be 0.1565 between 15° and 100° ; (4) show that the atomic mass, defined from Dulong and Petit's law, agrees with the atomic mass defined from considerations of isomorphism; (5) establish a simple method of estimation of vanadium.

Some Thallic Compounds.—V. Thomas.—The author believes that many of the thallic compounds hitherto accepted as definite are really mixtures of isomorphous compounds. This he proves to a certain extent.

Dioxy-tariric and Keto-tariric Acids.—M. Arnaud.—The oxidation of tariric acid—



either by MnO_4K or by nitric acid, gives a dioxy-tariric acid, $\text{C}_{18}\text{H}_{32}\text{O}_4$. In this case tariric acid behaves as stearic acid. The best method of causing the oxidation consists in the use of fuming nitric acid and stopping the rapid action by sudden cooling. After washing the crude product with water, the dioxy-tariric acid can be purified by crystallisation from concentrated alcohol. The yields are satisfactory. The acid is in the form of thin brilliant plates of a pale yellow colour, melting at 98° . Analysis proves the formula to be $\text{C}_{18}\text{H}_{32}\text{O}_4$.

Products of Condensation of Tetramethyldiamidobenzhydrol with some Primary Aromatic Amines with the Para-position occupied.—A. Guyot and M. Granderye.—The authors prepare, by condensing the primary aromatic amines having the para-position occupied with tetramethyldiamidobenzhydrol in dilute hydrochloric acid, not the products which theory would seem to suggest, but bodies of abnormal condensation—leucoauramine and azomethinic compounds.

New Reactions of Organo-metallic Derivatives.—E. E. Blaise.—By the use of organo-zinc compounds the author was enabled to prepare the primary β -oxy acids, mono- or di-substituted in α , oxy-acids of which scarcely any representatives are known, and hydracrylic acid. This method also allows of the preparation by simple dehydration of the non-saturated acids which correspond to the mono-substituted α oxy-acids.

Compounds of Alcohol with the Chlorides of Manganese and Cobalt.—F. Bourion.—The author obtains two new compounds of cobalt and manganese with alcohol, and determines several physical properties of these bodies. He also finds a means of separating cobalt and nickel by the solubility of their anhydrous chlorides in alcohol.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxv., No. 14.

A Sample of Crystallised Lime.—A. Jouve.—Already noticed.

Condensation of Cetipic Ether with the Orthodiamines.—R. Thomas-Mamert and A. Striebel.—The authors give the results obtained by the condensation of cetipic ether with orthophenylenediamine and its derivatives and some tetramines. They include benzoquinoline-diethylate of ethyl; the action of ethylate of sodium; the constitution of benzo- β -ketopentamethylene-azinemethyloate of ethyl; the action of carbonate of sodium in solution on benzo- β -ketopentamethylene-azinemethyloate of ethyl; benzo- β -ketopentamethylene-azinemethyloic acid; and many other bodies.

The Nitrated Bases in Roumanian Petroleum.—Dr. A. B. Griffiths and N. J. Bluman.—Roumanian petroleum is composed of hydrocarbides of various series, such as methane, ethylene, acetylene, and benzene, as well as cyclohexanes or saturated cyclic hydrocarbides, $(\text{C}_n\text{H}_{2n})$. The authors have recently analysed a sample of raw Roumanian petroleum of $\text{D}_{15} = 0.8445$, and they found the following products:—

	Per cent.
Benzine	10.65
Illuminating oil (1st quality) ..	61.20
" " (2nd quality) ..	20.08
Paraffin	2.83
Coke and loss	5.24

These figures justify the praise which has been bestowed on Roumanian petroleum, as a raw petroleum yielding 81 per cent of illuminating oil should be the basis of an important industry. The authors agree that this petroleum contains very little oxygen (less than 1 per cent), and they have recently discovered a basic nitrated compound in it having the odour of pyridine. This was effected by shaking up the petroleum with a 24.5 per cent aqueous solution of sulphuric acid. From this mixture, after adding an alkali and extracting with ether, they obtained a deep brown coloured, thick, oily liquid, boiling at 117° . This substance is very slightly soluble in cold water (pyridine is easily soluble); it is, however, soluble in ether, alcohol, benzene, and the mineral acids. It gives a crystalline precipitate with chloride of platinum and with ferrocyanide of potassium. The analysis of this body when purified gives the following results:—

	I.	II.	III.
Carbon	75.3	75.0	75.8
Hydrogen	6.8	6.6	6.5
Nitrogen	17.9	—	17.7

By treating a warm alcoholic solution of this substance with metallic sodium they obtained piperidine ($\text{C}_5\text{H}_{11}\text{N}$). This proves that the substance is pyridine ($\text{C}_5\text{H}_5\text{N}$) or a substance analogous to it.

A Biochemical Differentiation of the two principal Ferments in Vinegar.—G. Bertrand and R. Sazerac.—The authors have observed a very distinct differential character between two species of acetic ferments they often meet with, viz., the bacteria of vinegar (*Mycoderma aceti*) and the bacteria of sorbose (*Bacterium xylinum*). The first species is of the type of a ferment. Two samples of this, from different sources, have been examined, and they differ very slightly one from the other. Conical vessels containing 50 c.c. of broth, with 0.5 per cent of yeast and about 2.5 c.c. of alcohol, were infected and kept at a temperature of 28° . The acetic acid found was as follows:—

	Six days. Grms.	Ten days. Grms.	Seventeen days. Grms.
Microbe from Orleans	1.53	2.81	2.45
Microbe from Paris ..	1.43	2.35	2.52

The second species, from sorbose, was sown in a broth containing glycerin and peptone, and after two or three days a liquor was obtained precipitating Fehling's solution in the space of a few seconds; it oxidises the glycerin and forms dioxyacetone or propanediolone.

The Sensitiveness of the Methods for Detecting Salicylic Acid in Wines.—A. J. Ferreira da Silva.—After discussing various methods for detecting salicylic acid in wines, the author comes to the conclusion that the official German method is the best. The results obtained by four different methods are set out in a table.

Method of Preparation of the Lower Brewery Yeasts having the Property of Fermenting at a High Temperature, and How to Use them.—Georges Jacquemin.—Up to the present the methods of making beer could be divided into two great classes, according to whether the yeast was "high" or "low." The low yeasts are always used at a temperature below 10° , while the high yeasts are always used at a temperature above 10° . The beers obtained by the low fermentation have always a tendency to re-ferment if kept at a higher temperature than that of the original fermentation. The author has succeeded in modifying the conditions of existence of all the low fermentation yeasts, making them acquire the property of fermenting at a high temperature, even above 20° , while retaining in the beer the characteristic qualities demanded by the public.

MISCELLANEOUS.

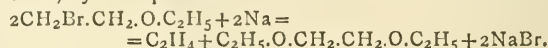
Dionine.—This is simply a fancy name for ethylmorphine hydrochloride, which was first prepared many years ago by the French chemist Grimaux. The alkaloid and the salt are regularly prepared by British manufacturers, and sold under their proper systematic names. Ethylmorphine is a homologue of codeine (methyl morphine), and has been shown by Professor Stockmar and others to have the same physiological action.

Directory of Paper-Makers.—We have received a copy of the above Directory for 1902, published by Marchant, Singer, and Co. The lists of paper-makers of the United Kingdom, under all the various headings, have been carefully and authentically revised to date. Additions have been made to the list of trade designations used as water-marks, &c., in papers, stationery, &c., bringing the total to over 4000; this feature will be of very great value to printers and stationers. There is also a complete classification of advertisers, forming a directory of paper-makers' principal engineers, purveyors of raw materials, paper mill suppliers, &c.; the whole making a useful book of reference for the trade.

On Pilocarpine.—A. Pinner and E. Köhlhammer.—The permanganic oxidation of pilocarpine eliminates the whole of the nitrogen from this base in the form of ammonia and methylamine, and gives a bibasic acid, $C_8H_{14}O_6$, of which the salts lose one molecule of water by the action of heat, and then correspond to a bibasic acid, $C_8H_{12}O_5$. $C_8H_{14}O_6$ is pulvic acid. Peroxide of hydrogen reacts on pilocarpine in the same way as permanganate. The sulphochromic mixture only reacts at the temperature of the water-bath, and gives pilocarpeic acid, $C_{11}H_{16}N_2O_5$. According to the authors, pulvic acid would be identical with the acid $C_7H_{10}O_4$ of Jowett (*Proc. Chem. Soc.*, vol. xvi., p. 124), and with the pyridinotartaric acid of Hardy and Calmels. Pulvic acid gives a deliquescent salt of potassium, $C_8H_{12}O_6K_2$ ($C_8H_{10}O_5K_2$ at 100°):— $C_8H_{12}O_6Ag_2$, $C_8H_{12}O_6Ba$ loses $\frac{1}{2}H_2O$ at 180° ;— $C_8H_{10}O_5(C_2H_5)_2$ boils at $181-183^{\circ}$ under 26 m.m. pressure, and 293° at 755 m.m. pressure. Pilocarpeic acid, $C_{11}H_{16}N_2O_5 \cdot H_2O$, is gummy, and fuses at $<100^{\circ}$.—*Berichte*, vol. xxxiii., p. 2357.

Action of Metallic Sodium on the Bromised Ethers.—B. N. Menschoutkine.—The author has examined the action of metallic sodium on the ethers $CH_2Br \cdot CH_2 \cdot O \cdot C_2H_5$ and $CH_2Br \cdot CH_2 \cdot CH_2 \cdot O \cdot C_2H_5$, prepared by the method he devised in collaboration with M. Volhof, and which consists of reacting with $ZnBr$, ZnO , or even CaO on alcoholic solutions of the dibromides. These bromised ethers are liquids of an agreeable odour; bromomethyl ether boils at $127-128^{\circ}$ $d_4^{20} = 1.3956$, for bromopropyl

ether, boiling at $149-150^{\circ}$ $d_4^{20} = 1.2697$. The reaction of metallic sodium on these bodies in ethereal solution commences without the application of heat; an abundant evolution of gas takes place, and the temperature rises; this action ceases after about twenty-four hours. The mixture, after standing for several days at the ordinary temperature, is heated on the water-bath, and the gases given off were recognised as being ethylene or propylene, according to which ether was used. The liquid products formed are principally ethylic ethers of the ethylenic and propylenic glycols, but there are also portions having a higher boiling-point which appear to contain the ethylic ethers of the tetramethylenic and hexamethylenic glycols. The principal reaction can be expressed (for bromomethyl ether) by the equation:—



—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 355.

The Separation of Aluminium and Glucinum by means of Hydrochloric Acid.—F. S. Havens.—The author, in collaboration with Mr. Gooch, has shown that hydrated chloride of aluminium is insoluble in ether saturated with hydrochloric acid, and that Fe_2Cl_6 is not; this allows of the separation of the two metals. Aluminium can be separated from glucinum in a similar way; the two metals being brought to the state of chlorides, half the volume of ether is added to the aqueous solution; this is then saturated with hydrochloric acid gas, and half the volume of ether again added, and the mixture again saturated with hydrochloric acid. In this manner a crystalline precipitate of $Al_2Cl_6 + 12H_2O$ is obtained, which is collected on an asbestos filter, and washed with ether saturated with hydrochloric acid gas. This precipitate is dried at 150° , then calcined progressively under a layer of pure mercuric oxide; the alumina is finally weighed. This latter is free from glucinum; as for the glucinum, it is found entirely in the filtered ethereal liquor. After having driven off the whole of the ether and the free hydrochloric acid by evaporation, the glucina can be estimated, either by precipitating with NH_3 or by evaporating the solution containing the $GICl_2$ with nitric acid, and then calcining the nitrate formed.—*Zeit. Anorg. Ch.*, vol. xvi., p. 15.

NOTES AND QUERIES.

Note on the Cleansing of Mercury.—The necessity of having clean mercury for an experiment led me to try the methods suggested in "Thorpe's Dictionary of Chemistry." These are—(a) The use of sugar, (b) very dilute nitric acid, (c) sulphuric acid as digesting agents. The first method was not only bothersome, but a failure. Even dilute nitric acid attacks the metal after a time. Sulphuric acid, however, proved quite successful. Digestion with strong sulphuric acid (1:8) is an excellent method of cleansing mercury, and after three or four digestions with it, dilutions, and filtrations, even the dirtiest mercury is cleansed.—FRANCIS GEORGE COUSINS, Golding Grammar School, Kent.

Lecture Experiments on the Nature of Solution.—First show the solution of hydrogen chloride in water and the resulting elevation of temperature and increase in volume. Secondly, passing steam into water, show that here also there is increase in volume and elevation of temperature. Next, pointing out the striking resemblance between the two experiments, show that solution is merely change of state effected by means of a liquid; in other words, that Black's theory is quite correct.—FRANCIS GEORGE COUSINS.

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THE CHEMICAL NEWS.

VOL. LXXXV., No. 2210.

THE EFFECT OF LIME ON THE INSOLUBLE PHOSPHATES IN SOILS.

By WALTER F. SUTHERST, Ph.D., A.I.C.

THE importance of adding lime to land and its many advantages are, of course, well known to every farmer, but one of its effects seems to be overlooked, viz., its action on those phosphates which are generally considered valueless as plant foods, *e.g.*, those of iron and aluminium. These occur in nearly every soil, and are of two sources: one being from the disintegration of rocks containing vivianite (ferrous phosphate) and wavellite (aluminium phosphate), the other source being a result of the reversion of superphosphate of lime added to soils containing oxides of iron and aluminium.

Phosphates of calcium (that is, the tri- and di-), though insoluble in water, are, nevertheless, not valueless as plant foods, since the weakest acids, such as carbonic and the acids in the roots of plants, are capable of dissolving them, and thus rendering them capable of absorption. Since the phosphates of iron and aluminium are insoluble in carbonic, and very sparingly soluble in organic acids, their food value is comparatively small, and a long time is needed before they could be absorbed by the root saps.

The method usually employed in England for determining the value of neutral phosphates is that recommended by Dr. Bernard Dyer, and consists in treating the phosphate in question with a 1 per cent solution of citric acid (this strength being the nearest to the acidity of the root saps); and this method I have used in the determinations carried out.

To show the relatively low value of the iron and aluminium phosphates as such, the solubilities of these were first determined as follows:—

One gram. each of ferrous, ferric, and aluminium phosphates were placed in a small flask containing 100 c.c. distilled water, and to each was added 1 gram. citric acid, then allowed to stand twenty-four hours with occasional shaking. At the end of that time the liquid was filtered off, the residue well washed with distilled water, and in half the filtrate (= 0.5 gram. substance) the soluble phosphoric acid was determined by adding ammonium molybdate and nitric acid and heating on the water-bath three hours. After cooling, the clear supernatant liquid was filtered off and the residue washed four times by decantation with 2½ per cent nitric acid. The precipitate was then dissolved in ammonia and to this magnesia mixture added, and after standing three hours the ammonium-magnesium phosphate filtered off, washed with 2½ per cent ammonia, the filter and contents placed in a platinum crucible, and ignited first over the Bunsen flame and finally over the blowpipe.

0.5 gram. $\text{Fe}_3(\text{PO}_4)_2$ gave 0.0388 gram. $\text{Mg}_2\text{P}_2\text{O}_7$, equal to 2.475 per cent P_2O_5 dissolved.

0.5 gram. $\text{Fe}(\text{PO}_4)_2$ gave 0.0432 gram. $\text{Mg}_2\text{P}_2\text{O}_7$, equal to 2.755 per cent P_2O_5 dissolved.

0.5 gram. $\text{Al}(\text{PO}_4)$ gave 0.0502 gram. $\text{Mg}_2\text{P}_2\text{O}_7$, equal to 3.203 per cent P_2O_5 dissolved.

The three phosphates on analysis contained as total phosphoric acid:—(1) Ferrous phosphate, 25.924 per cent P_2O_5 ; (2) ferric phosphate, 23.255 per cent; (3) aluminium phosphate, 28.680 per cent. The proportion of citric acid-soluble phosphoric acid to total would be—

$\text{Fe}_3(\text{PO}_4)_2$	..	..	..	..	10.64
$\text{Fe}(\text{PO}_4)_2$	..	..	..	..	10.62
AlPO_4	..	..	..	..	11.16

When slaked lime is allowed to act on the above phosphates in the presence of water, the greater part of the phosphoric is rendered soluble in citric acid, especially in the case of the ferric phosphate (the one most commonly found in the soil), the lime evidently combining with the phosphoric acid, setting free hydrates of iron and aluminium; the change of the light yellow ferric phosphate to a reddish brown precipitate proving this decidedly.

The action of lime was carried out experimentally as follows:—One gram. of the phosphate was placed in a small flask and mixed with 100 c.c. distilled water, then 2 grms. pure slaked lime added; the contents of each flask then well agitated and allowed to stand for periods of twenty-four, forty-eight, and seventy-two hours with constant shaking. At the end of twenty-four hours 1 gram. of citric acid was added to three of the different phosphates, and the calculated amount of citric acid necessary to neutralise the excess of lime present, and after standing twenty-four hours filtered off, and the dissolved phosphoric acid estimated as above. The following results were obtained:—

Time. Hours.	$\text{Mg}_2\text{P}_2\text{O}_7$. Grms.	Equal to P_2O_5 .	Proportion of soluble to total P_2O_5 .
I. Ferrous Phosphate.			
24	0.1532	19.55	75.42
48	0.1736	22.15	85.45
72	0.1746	22.26	85.88
II. Ferric Phosphate.			
24	0.1721	21.96	94.45
48	0.1756	22.41	96.38
72	0.1760	22.45	96.55
III. Aluminium Phosphate.			
24	0.1441	18.45	64.33
48	0.1558	19.88	69.31
72	0.1564	20.65	72.00

In the same manner experiments were tried using calcium carbonate instead of slaked lime, but in no case, even at the end of fourteen days, was there any increase in the solubility.

From the above results it will be seen that it is essential that the lime should be in the form of hydrate, the carbonate being of no value whatever. Since lime is often applied to land in a very careless manner, it naturally follows that the beneficial effects of it are often lost. If left exposed for a long time to the air, it changes slowly to carbonate, due to absorption of carbonic acid from the air and rain, and much is lost in this way when the lime is air-slaked. Too much stress cannot be laid on this matter, and all farmers should take care to spread the lime as soon as it has crumbled to powder.

The Cheshire Agricultural College,
Holmes Chapel.

On Certain Regular Relations Observed in the Distillation of Dilute Aqueous Solutions of Phenol.

—Al. Neumann and W. Muller.—Five hundred c.c. of an aqueous solution of phenol of known strength are boiled for thirty minutes, and care is taken to keep the volume constant by adding water by means of a funnel fitted with a tap; the phenol contained in 100 c.c. of the liquid which passed over during this thirty minutes distillation is then estimated. By repeating this experiment on solutions of different strengths, the authors found that 100 c.c. of the distillate constantly contained three times less phenol than the 500 c.c. of solution at the commencement of the distillation, and they calculate from this that at 100°, near the surface of the boiling solution, the proportion of phenol in the vapour should always be double the amount of that in the liquid at equal volumes.—*Berichte*, vol. xxxiv., p. 224.

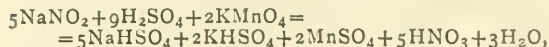
THE
OXIDATION OF NITRITE BY PERMANGANATE.

By JOHN WADDELL, B.Sc. (Lond.).

IN the titration of a nitrite by potassium permanganate it is usual to add a large excess of sulphuric acid. The oxidation may therefore be considered as an oxidation of nitrous acid to nitric acid.

It happened to be a matter of interest to me to learn whether excess of acid is necessary, or whether a nitrite can be oxidised to a nitrate. As I found nothing on this point in the literature of the subject I carried out the following little investigation with sodium nitrite:—

I started out on the assumption that the reaction between sodium nitrite and potassium permanganate in acid solution is represented by the equation—



and weighed out the reagents accordingly, taking roughly 10 grms. of sodium nitrite, 26 grms. of sulphuric acid, and 9 grms. of potassium permanganate, each of these quantities being dissolved in water, and the solutions being made up to a litre.

The permanganate was standardised against Mohr's salt; 4 grms. of Mohr's salt required 36.3 c.c. of the permanganate solution, which therefore contained 8.883 grms. solid permanganate per litre. The nitrite was then titrated against the permanganate in two ways. In the first titration 3 c.c. or 4 c.c. of sulphuric acid was added to water, and the solution cooled; then about 25.5 c.c. of permanganate solution added, and the whole made up to approximately 100 c.c. This acidulated permanganate was added to 24.9 c.c. of nitrite also diluted to 100 c.c. From previous trials these quantities were known to be approximately equivalent. The permanganate was completely decolorised, and more was added from the burette until a pink colour was obtained which lasted for ten minutes. The total amount of permanganate was 26.2 c.c.

Another titration was made in accordance with Lunge's method for estimating nitrous fumes dissolved in sulphuric acid. About 7 c.c. of strong sulphuric acid was added to about 100 c.c. of water, the temperature becoming 40° C.; 20 c.c. of permanganate was added to this, and then nitrite was run in. The decolorising took a few seconds, and I found I had very slightly overshot the mark, and needed to add 0.25 c.c. permanganate in order to bring back the pink colour. In this test 20.25 c.c. permanganate were decolorised by 19.30 c.c. nitrite.

The two titrations gave:—

$$\begin{array}{l} 1 \text{ c.c. nitrite} = 1.0522 \text{ c.c. permanganate} \\ 1 \text{ " " " } = 1.0493 \text{ " " " } \end{array}$$

$$\text{Mean} \dots 1.0507$$

and the solution of nitrite contained 10.190 grms. sodium nitrite per litre.

The sulphuric acid was estimated by precipitating with barium chloride, and proved to contain 25.74 grms. H_2SO_4 per litre.

A few preliminary experiments showed that the sulphuric acid necessary was much less than required by the equation at first assumed. The most satisfactory method of procedure was found to be to add the mixture of acid and permanganate to the nitrite; when the nitrite was added in the cold to the permanganate a muddy precipitate of manganese hydroxide was formed which was difficult to get rid of. At 40° C. there was not so much precipitate on adding the nitrite to the permanganate, and the result of one determination in this way is given.

To 26.15 c.c. permanganate 8.75 c.c. sulphuric acid was added, and water to make up to about 100 c.c., and the temperature was raised to 40° C. When nitrite was run in, the liquid became muddy, but on the addition of 24.80

c.c. of nitrite the precipitate soon settled, leaving the supernatant liquid colourless. There was considerable deposit of hydroxide, which became less, but did not entirely disappear at 60° C. The liquid was practically neutral, but became acid on addition of 0.2 c.c. acid, and after a few hours the residue almost entirely disappeared.

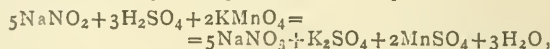
Though according to Lunge, when excess of acid is present, it is better to add the nitrite to the acidified permanganate, for my purpose the converse process was preferable, and my final experiment was the following:—

8.75 c.c. of sulphuric and 25.88 of permanganate were added to 100 c.c. of water at 40° C., and a little of this mixture added to 25 c.c. of the nitrite. A muddiness was produced, and a few drops more of acid were added, making in all 8.9 c.c. The nitrite was slightly warmed, and then all of the permanganate mixture was added. The liquid became clear and colourless. A little more permanganate was added from the burette, no additional acid being put in. The colour took some minutes to disappear. The last addition was 0.2 c.c., and the colour did not disappear after ten minutes. There was a very slight cloudiness; the liquid was neutral. As the last addition of permanganate seemed to be a slight excess, I assumed that 0.1 c.c. would have been enough to add. This would have made a total of 26.18 c.c. of permanganate for 25 c.c. of nitrite, or 1 c.c. nitrite = 1.0472 c.c. permanganate; a result not far from that obtained with a large excess of acid.

The actual amounts by weight of the reagents was:—

$$\begin{array}{l} 0.2325 \text{ grm. permanganate} \\ 0.2547 \text{ grm. nitrite} \\ 0.2291 \text{ grm. sulphuric acid} \end{array}$$

This very nearly corresponds with the equation—



according to which 0.2325 grm. of permanganate would require 0.2537 grm. of nitrite and 0.2162 grm. of sulphuric acid.

It appears, therefore, that it is not necessary to add more acid than just enough to make neutral sulphates and nitrates.

School of Mining, Kingston, Canada.

A NEW METHOD FOR THE ESTIMATION OF GOLD AND SILVER IN PYRITES.

By W. BUDDÉUS.

THE usual methods are scorifying with lead in small dishes in a muffle, or fusing with lead and a flux, then cupelling in both cases. The first of these methods is the most exact, but it is expensive on account of the large amount of material used and the time required. Even very satisfactory results are too low, however, up to a certain point, because of the volatilisation due to the high temperature of the muffle, and also because some of the precious metal remains fixed in the regulus which is always formed between the lead and the slag.

In this new method the sample is ground sufficiently fine to pass through a sieve having 300 or 400 meshes per square centimetre; 100 grms. of an ore containing 50 grms. or more of gold per 1000 kilos., or 200 grms. for ores which contain less than 50 grms. per 1000 kilos., are placed in a crucible, preferably one of white Paris clay, of 70 or 130—140 c.c. capacity, according to the weight of the sample taken.

The crucible is lightly covered and placed in a muffle heated to redness, for half to three-quarters of an hour, until all trace of the sulphur flame disappears. It is placed on a sheet of iron to cool, and the contents then emptied into a glass vessel or porcelain dish of 1 or 2 litres capacity.

The roasted ore, which is principally sulphide of iron, is only loosely aggregated, and can be easily detached from the crucible, and the dust brushed out with a camel-hair brush.

It may be stated, generally, that the mass has taken the form of the interior surface of the crucible, but it need not be broken up. It is then treated with a mixture (250 or 500 c.c.) of hydrochloric acid free from arsenic, with its own volume of water. After standing for about an hour in a warm place, another 250 or 500 c.c. of the acid mixture are added, and the whole boiled for some time. The sulphide of iron, which formed eight-ninths of the whole mass, is dissolved rapidly, leaving behind the whole of the gold and silver, with the silica and clay of the gangue.

When the sulphide is completely decomposed, the solution is diluted with water until the crucible or dish is nearly full; it is then filtered.

The residue is washed two or three times with water, then dried, transferred, with the filter-paper, to a Hessian crucible of 150 or 300 c.c. capacity, mixed by means of a spatula with 50 or 100 grms. of assay lead and 5 or 10 grms. of borax, and finally fused in the muffle. It is of advantage to use 100 or 200 grms. of a mixture of equal parts of acetate of lead and caustic soda, instead of assay lead.

After cooling, the crucible is broken, the lead is detached and cupelled immediately; the gold and silver are then parted in the usual manner.

The cost of an assay of 200 grms. of ore, according to the old method, which necessitates the use of 1400 grms. of pure lead at 1 mark 20 pfennigs per kilo., besides the scorifying dishes and cupels, and allowing 1 mark for heating, &c., is 1 mark 88 pfennigs; while, by the new method, which only requires 500 c.c. of hydrochloric acid, 100 grms. of assay lead, and a crucible, the cost, including the heating, &c., varies from 37 pfennigs to 72 pfennigs.

The results are perfectly accurate and concordant among themselves; check assays never differ by more than 1 m.grm.

The results, as proved by comparative assays, are uniformly higher than those obtained by the old method.—*Chemiker Zeitung*, xxiv., p. 922.

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

WE wish to draw the attention of our readers to the fact that the Fifth International Congress of Applied Chemistry will take place at Berlin during the Whitsuntide Holidays in 1903, under the Presidency of Dr. Clemens Winkler. The House of the Imperial Parliament (Reichstag) has been placed at the disposal of the Congress, and Geheimrath Professor Otto N. Witt has been nominated President of the Organising Committee; Dr. Bottinger, Member of the German Parliament, acting as Treasurer. A fund of about £3000 has already been collected by voluntary subscriptions from societies and private individuals towards the expenses of the Congress.

The object of these Congresses is to further the interests of "Applied Chemistry" in the widest sense of the words. They embrace both Industrial and Analytical Chemistry; in the latter department one of the chief objects is to enable chemists to decide on standard methods for the testing and assaying all kinds of chemical products and raw materials, and to bring about international agreements for the employment of the selected processes. Much useful work has already been effected in this direction at the former Congresses held in Paris, Brussels, Vienna, and again in Paris.

Great interest has been taken in these meetings by different Continental Governments, and an official representation may be expected on the part of some of them on the forthcoming occasion.

The absence of many English chemists on previous occasions has been much remarked, although this probably arose from the Congresses not being better known. It would seem to be greatly to the advantage of English science that this nation should be well represented at Berlin. Probably the best commencement would be for some of the leading chemists to form a committee for carrying out the preparatory work needed to enable this country to take its rightful place among the nations who will be represented at Berlin next year. We should think that the selection of such a committee would fall well within the scope of the British Association, and it is to be hoped that under the auspices of so eminent a chemist as Professor Dewar, the President, a representative committee with this object will enter into existence during the Belfast Meeting.

ON THE FUSION OF QUARTZ IN THE ELECTRIC FURNACE.*

By R. S. HUTTON, M.Sc.

DURING recent years a good deal of attention has been paid to the working of fused quartz with a view to its use in the construction of apparatus. (*Vide* C. V. Boys, *Phil. Mag.*, 1887; H. L. Callendar, *Journ. Iron and Steel Inst.*, 1892, i., 165; W. Crookes, "On the Spectra of Argon," *Phil. Trans.*, 1895, 186 (A), 245; R. Threlfall, "Laboratory Arts," 1898, esp. p. 199; A. Dufour, *Comptes Rendus*, 1900, cxxx., 775; A. Gautier, *Comptes Rendus*, 1900, cxxx., 816; W. A. Shenstone, *Nature*, 1900, lxi., 540; W. A. Shenstone and H. G. Lacell, *Nature*, 1900, lxii., 20; W. A. Shenstone, *Proc. Roy. Inst.*, 1901; *Nature*, 1901, lxiv., 65 and 126).

Owing to the exceedingly small coefficient of expansion of this material (H. Le Chatelier, *Comptes Rendus*, 1889, cviii., 1046, and 1900, cxxx., 1703; H. L. Callendar, *vide* Shenstone, *Nature*, 1901, lxiv., 66), and to its high melting-point, it would doubtless find many applications for making vessels in which to study the properties of substances at high temperatures, and especially for making high temperature gas thermometers. Further, since fused silica withstands very sudden changes of temperature without showing any tendency to crack, probably many industrial uses could be found for it as soon as a more economical method of fusing and working it is forthcoming. Up to the present, the oxyhydrogen blowpipe has been used almost exclusively, and, in the hands of Shenstone and Lacell and of Dufour, has led to very satisfactory and promising results. The process is, however, expensive, and is also very slow, since the oxyhydrogen flame is at a temperature only slightly above the fusing-point of silica, and, in fact, it is only at a certain point in the flame that the fusion can be carried out at all.

Moissan ("Le Four Electrique," 1897, p. 49; A. Gautier, *Comptes Rendus*, 1900, cxxx., 816) has studied the effect of the electric arc upon silica, and has noted that it fuses, and is easily volatilised; but he studied more particularly the reduction products, carborundum and silicon, which remain behind when silica is heated for some time in an electric furnace, and, according to Gautier, did not succeed in making apparatus of this material. Upon repeating Moissan's experiment on the volatilisation of flint stones as a lecture experiment with an electric-arc furnace using 300 ampères at 50 volts, I was struck by the appearance of the residual unvolatilised silica, which was very glassy and in parts quite transparent. Experiments soon showed that, provided a small current of air is allowed to pass through the furnace, no reduction of the solid or liquid silica takes place, and, consequently, the arc can be used as a source of heat for fusing silica without fear of reduction spoiling the results.

* Read before the Manchester Literary and Philosophical Society, January 7th, 1902.

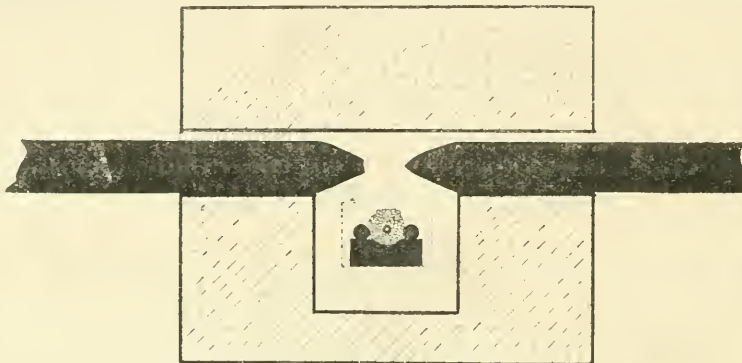
At first apparatus was fitted up for obtaining an arc flame from inclined carbons by magnetic deflection downwards; in this way the arc flame was made use of much in the same manner as the oxyhydrogen flame, and rods could be made easily by the method recommended by Shenstone. It was soon found, however, that a small arc using 15–20 ampères was not sufficiently powerful to ensure rapid work, and after working with a similar open arc, using about 50 ampères with separate circuit for the magnet, the furnace was again brought into use for fusing the quartz.

Whilst employing the open arc, however, several interesting observations were made, which may be worth while recording.

In the first place, supports of carbon can be used with advantage for bringing the quartz into the flame, but it is necessary that the carbon used for these supports, as also the carbons used for the arc, be as pure as possible, or else the quartz may be contaminated by the ash which falls upon it; for the supports I have throughout made

In this way one certainly makes more use of the heat of the arc, since the reflection from the cover prevents a great part of the heat being lost, and magnetic deflection of the arc, which in this case was not made use of, might be found a further advantage for economical working.

A current of about 300 ampères at 50 volts was usually employed, and with this power the quartz was seen to melt on the surface within a minute or so of commencement. Nearly all the experiments with this form of furnace were arranged with a view to preparing thick-walled tubes of quartz, with a core of about $\frac{1}{4}$ inch. As seen from the figure, a rough mould was made of carbon with a carbon core, resting at each end on carbon supports. The mould was arranged usually for making tubes 10 to 12 inches long, but, obviously, any desired length of tube could be similarly constructed. The mould was filled with broken-up quartz of different degrees of fineness, but it was found that the best results were obtained when the quartz was not too finely powdered. The tubes obtained in this way can easily be separated from the carbon support and the



SECTION OF ELECTRIC FURNACE. (One-fifth natural size).

use of graphitic carbon prepared in the electric furnace, which is very pure and easy to work; it can, moreover, now be obtained on the market at a reasonable price.

In building up small rods, grooves were cut in a plate of this carbon, and small pieces of prepared quartz were placed in these grooves, the quartz being melted together gradually from one end to the other of the grooves, by sliding the carbon plate gradually under the arc-flame. Small lens-shaped discs can be similarly prepared by placing pieces of the prepared quartz in a shallow carbon crucible, and, with a little practice, it is hoped that masses suitable for making lenses can be prepared in this way. The valuable optical properties of fused quartz are pointed out by Shenstone in his papers.*

When quartz is thus fused in the arc, it is quite easy to observe the reduction which takes place in the immediate neighbourhood of the arc, and causes a black stain on the surface, which can easily be made to disappear by bringing the heated mass for a short time away from the centre of the flame; in fact, the working of quartz in the arc-flame much resembles the working of lead glass in the ordinary blowpipe, except for the immense difference of temperature.

Owing to insufficient skill in the art of glass-blowing, and to the pressure of other work, I did not feel encouraged to proceed with these experiments with the open arc, but undertook a few experiments with the furnace which have led to promising results.

A Moissan arc furnace of the well-known type was modified by cutting passages in the sides, so that a carbon support charged with quartz could be passed under the arc and at right angles to it; a section of the furnace is seen in the accompanying figure.

* It should be mentioned that Messrs. Zeiss, of Jena, exhibited small lenses at the Paris Exhibition in 1900, made of "crystal de roche fondu," but the method by which the quartz was fused was not stated.

core be withdrawn, since the silica does not adhere to the carbon.

Up to the present, I have not succeeded in preparing tubes quite free from bubbles, but the general appearance can be greatly improved by re-heating under the arc, preferably with mechanical rotation in order to get a more uniform result. Even in their present form, however, they would probably be of much use for constructing apparatus, as, owing to their thickness, there is plenty of material for blowing and drawing down purposes, and by this process the appearance of the material is, of course, much improved.

Pure white sand fused in a similar way always seems to give a much more opaque mass; but plastic quartz can take up a certain amount of sand without thereby impairing its transparency, and probably a small sand blast, blowing sand or fine quartz, could be used for thickening bulbs and tubes of quartz fused by this method.

It is to be hoped that those who have large power at their disposal will extend the application of this method, which may thus bring fused quartz apparatus within the reach of those wishing to make use of it in virtue of its interesting and valuable properties.

The experiments described in this paper were carried out in the Physical Laboratories at Owens College.

Research on Lactic Fermentation from observations of Electric Resistance. — MM. Lesage and Dongier. — Ostwald's apparatus, which allows of the measurement of electric resistance of liquids by Kohlrausch's method, can be utilised for the study of milk fermentation. It is found that the diminution in resistance is progressive, and the rapidity of the variation often changes, according to whether the milk is kept in closed or open vessels. — *Comptes Rendus*, cxxxiv., No. 10.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19th, 1902.

Prof. J. EMERSON REYNOLDS, Sc.D., V.P.R.S., President,
in the Chair.

MESSRS. Catchpole, Green, and Hanson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George H. A. Clowes, Gratwick Research Laboratory, Buffalo, U.S.A.; Henry Crookes, 109, Ladbroke Grove, W.; Walter Everitt, 83, The Grove, Ealing, W.; J. Arthur Gill, 19, Burma Road, Stoke Newington, N.; John T. Griffiths, Grammar School, Hanley Castle, Worcestershire; Sidney Isaac King, 49, Arundel Square, N.; Robert Mathieson, Rillbank, Innerleithen, Peebleshire; George Augustus Henry Mence, Ouse Villa, St. Ives, Hunts; Thomas Taylor, 12, Ancaster Drive, Great Western Road, W.; Frank Stanley Wood, 25, Suffolk Street, Newland, Hull.

The SECRETARY announced that the Treasurer, Professor TILDEN, had represented the Society at the recent celebration of the Jubilee of The Owens College, Manchester, and had presented the following congratulatory Address from the Society:—

"The President, Council, and Fellows of the Chemical Society desire on this the present occasion of the celebration of the Fiftieth Anniversary of the foundation of Owens College to express their high appreciation of the conspicuous services rendered to the cause of scientific education by the foundation and ever increasing activity of the College.

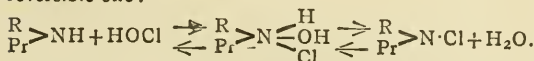
"They recall with especial satisfaction the contributions to Chemical Science which have emanated from the laboratories of Owens College under the direction of the successive eminent Professors of Chemistry who must be regarded as the immediate scientific successors of John Dalton, the founder of Modern Chemistry. With sincere wishes for the future development and extended usefulness of the College they desire to tender to the President, Council, Fellows, and Students an expression of hearty congratulation on the celebration of this their Jubilee.

J. EMERSON REYNOLDS, President.
WILLIAM A. TILDEN, Treasurer.
WYNDHAM R. DUNSTAN,
ALEXANDER SCOTT, } Secretaries."
RAPHAEL MELDOLA, }

Of the following papers, those marked * were read:—

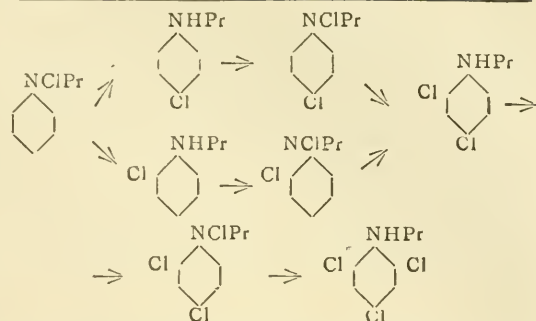
*43. "Nitrogen Chlorides containing the Propionyl Group." By F. D. CHATTAWAY.

Aniline and the chloro-substituted anilines readily yield propionyl derivatives, which, on treatment with excess of hypochlorous acid, are converted into substituted nitrogen chlorides. In these reactions, hypochlorites are probably first formed, the nitrogen developing its higher valency, water being subsequently eliminated. The reaction is a reversible one:—



These nitrogen chlorides show all the characteristic reactions of the group, the chief feature of such reactions being the invariable replacement of the halogen by hydrogen.

When there is hydrogen, either in the para- or the ortho-position, transformation of the nitrogen chloride into the isomeric substituted anilide readily takes place according to the scheme:—



The following compounds have been prepared:—

- Chloroimino-propionanilide*, $\text{C}_6\text{H}_5 \cdot \text{NCl} \cdot \text{COC}_2\text{H}_5$, colourless plates, m. p. 77° .
p-Chloropropionanilide, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{COC}_2\text{H}_5$, plates, m. p. 141° .
Chlorimino-p-chloropropionanilide, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NCl} \cdot \text{COC}_2\text{H}_5$, colourless plates, m. p. 55° .
Bromoimino-p-chloropropionanilide, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NBr} \cdot \text{COC}_2\text{H}_5$, yellow prisms, m. p. 71° .
o-Chloropropionanilide, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{COC}_2\text{H}_5$, colourless plates, m. p. 91° .
Chloroimino-o-chloropropionanilide, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NCl} \cdot \text{COC}_2\text{H}_5$, colourless plates, m. p. 57° .
Bromoimino-o-chloropropionanilide, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NBr} \cdot \text{COC}_2\text{H}_5$, pale yellow prisms, m. p. 106° .
2:4-Dichloropropionanilide, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NH} \cdot \text{COC}_2\text{H}_5$, colourless prisms, m. p. 121° .
Chloroimino-2:4-dichloropropionanilide, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NCl} \cdot \text{COC}_2\text{H}_5$, colourless plates, m. p. 64° .
Bromoimino-2:4-dichloropropionanilide, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NBr} \cdot \text{COC}_2\text{H}_5$, pale yellow rhombs, m. p. 66° .
2:4-Trichloropropionanilide, $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{NH} \cdot \text{COC}_2\text{H}_5$, colourless prisms, m. p. 161° .
Chloroimino-2:4:6-trichloropropionanilide, $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{NCl} \cdot \text{COC}_2\text{H}_5$, pearly plates, m. p. 80° .
Bromoimino-2:4:6-trichloropropionanilide, $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{NBr} \cdot \text{COC}_2\text{H}_5$, bright yellow plates, m. p. 106° .

*44. "The Constitution of the Metallic Cyanides as deduced from their Synthetic Interactions: the Constitution of Hydrogen Cyanide." By J. WADE.

The formation of both nitriles and isocyanides from metallic cyanides has been explained in three ways: (1) the metallic cyanides are iso-cyanides, and yield isocyanides by direct interchange; nitriles are formed subsequently by isomeric change; (2) hydrogen cyanide is tautomeric and forms two classes of metallic salts (Laar); (3) the metallic cyanides are isocyanides and yield isocyanides as in (1); nitriles are formed when the metal is highly positive by the intervention of additive compounds, such as $\text{K} \cdot \text{N} \cdot \text{Cl} \cdot \text{Et} = \text{KI} + \text{N} \cdot \text{C} \cdot \text{Et}$ (Nef).

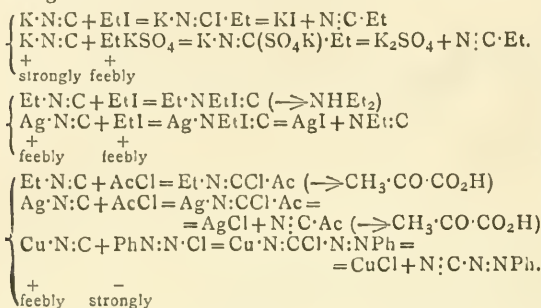
Further investigation of the conditions under which isocyanides are transformed into nitriles shows that the first of the above hypotheses is inadequate. The synthetic cyanides are thus independent and primary products. The tautomerism of hydrogen cyanide does not, however, account for the facts observed; these would necessitate the tautomerism of the metallic cyanides.

The third or additive hypothesis accounts for the dual action of potassium and similar cyanides. There is no evidence, however, that the action between silver cyanide and alkyl haloids is ionic in character, nor does the hypothesis account for the different action of alkyl and acyl haloids on silver and similar cyanides.

The action of alkyl iodides on silver cyanide is parallel to their action on alkyl isocyanides, the alkyl in each case

combining with the nitrogen of the cyanogen group, whereas in the action of acyl halogen compounds the acyl combines with the carbon. The alkyl radicles are feebly electropositive, the acyl electronegative; the additive power of the unsaturated carbon of the isocyanides is thus dependent not merely on the electrochemical character of the attached radicle, as Nef postulates, but on its electrochemical position relatively to the radicle of the interacting halogen compound.

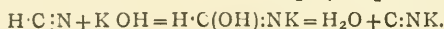
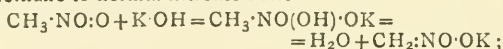
When the metal or alkyl of the isocyanide is sufficiently positive with regard to the radicle of the interacting molecule, the latter combines with the carbon of the isocyanogen group, but when the two radicles are electrochemically adjacent, the interacting molecule combines with the nitrogen:—



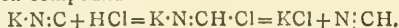
The principle of this hypothesis is applicable to other similar cases of dual action.

The reactions which indicate an isocyanic constitution for hydrogen cyanide are also susceptible of an opposite interpretation. The physical and physiological properties of hydrogen cyanide also correspond with those of the nitriles.

It is probable that the metallic cyanides are, as Gautier suggested, salts of a labile hydrogen isocyanide; their relation to ordinary hydrogen cyanide or formonitrile is similar to that of the salts of Hantsch's labile isonitromethane to normal nitromethane—



The labile isomeride could only be made from metallic cyanides by the action of acids. These necessarily contain electronegative radicles, and therefore combine with the carbon of the cyanide, yielding the normal or nitrilic hydrogen compound—



*45. "The Absorption Spectra of Metallic Nitrates." Part I. By W. N. HARTLEY, D.Sc., F.R.S.

Soret was the first to observe an absorption band in solutions of nitric acid and potassium nitrate, but Soret and Rilliet did not observe it in ethyl nitrate. The author made, in 1887, an extended examination of the absorption spectra of nitrates of the simplest constitution to see if he could find any difference corresponding to that observed by Bunsen in the salts of didymium (*Pogg. Ann.*, 1866, cxxviii., 100).

The results obtained by the author show that the curves of nitric acid and potassium nitrate are identical, but those from silver and thallium nitrates differ widely from one another and from that of nitric acid. In the case of nitric acid, the mean position of the band primarily due to NO_3 lay between λ 317 and 285. The general effect of silver nitrate is to cause an absorption of all rays beyond λ 340, but there is a feeble transmission of a line about λ 274. Thallium nitrate has an absorption band from λ 324 to 274. With a dilution of $N/1000$, there is still an absorption of the rays about λ 242, although water transmits the rays to λ 211.

The solutions were examined in two ways, namely—

(1) by using a fixed length of tube (200 m.m.) and varying the strength of the solutions, the best results being obtained with solutions between $N/20$ and $N/200$; (2) by using normal solutions and varying the length of tube.

With normal solutions and a 200 m.m. tube nitrates of the following transmitted a strong continuous spectrum to somewhere about λ 340, after which there was a complete general absorption.

H λ 346	Mg λ 357	Tl λ 340 ($N/4$)
Li 346	Ca 340	Ba 340 ($N/4$)
Na 340	Zn 346	Pb 346 ($N/2$)
K 346		
Ag 355		

46. "A Method of Determining the Ratio of Distribution of a Base between Two Acids." By H. M. DAWSON and F. E. GRANT.

The method consists in shaking up an aqueous solution containing two acids and a base (the latter being insufficient for saturation of the acids) with a second liquid which is but slightly miscible with water, and which is capable of extracting one and one only of the four substances present in the solution. Tartaric, malic, succinic, and citric acids are not extracted from their aqueous solutions by chloroform, but considerable quantities of acetic acid are.

Determinations of the ratio of distribution of acetic acid between water and chloroform at 20° have been carried out, and show that this ratio increases very considerably with the dilution. By means of a diagram on which the acetic acid concentrations are plotted as abscissæ, and the distribution coefficients as ordinates, the concentration of the acids in water corresponding to any given concentration in chloroform can be readily ascertained. The influence of the presence of the salts and the second acid on the distribution ratio of the acetic acid has been investigated and found to be small.

On shaking up an aqueous solution containing soda, acetic and tartaric acids, with chloroform, and determining the concentration of the acetic acid in the latter, then from the diagram the concentration of the free acetic acid in the aqueous solution can be ascertained. If the original concentrations of the base and the two acids are known, the concentrations of the free tartaric acid and of the two salts can be calculated.

The aqueous solutions were prepared in such a manner that after shaking up with an equal volume of chloroform, the base and the two acids were present in as nearly as possible equivalent quantities, the excess of acetic acid required in the original solution being determined from the preliminary distribution experiments.

Several series of experiments have been carried out in which acetic acid is compared with the several acids above mentioned, three or four concentrations being investigated in each case, and the ratios determined for the distribution of the base between acetic and each of these acids.

This method of determining the ratio of distribution of a base between two acids can also be employed where the second liquid takes up two of the components, for example, the two acids from the aqueous solution, but the ratios of distribution of the two acids between water and the second liquid must differ considerably from one another at any given concentration.

47. "On the Molecular Complexity of Acetic Acid in Chloroform Solution." By H. M. DAWSON.

The considerable increase of the ratio in which acetic acid distributes itself between water and chloroform with increasing dilution is shown to be due to a gradual dissociation of the double molecules present in the latter solvent into simple molecules.

The limiting concentrations at which distribution experiments have been carried out correspond to an almost complete change in the molecular complexity of the dissolved acid. At a concentration of 12 grms. per litre of chloroform, the acetic acid present in the form of double molecules is about five times as great as that in the form

of simple molecules, whilst at a concentration of 0.1 grm. per litre the proportion is only one-fifth.

The formation of double molecules by substances containing the hydroxyl group, when dissolved in liquids not containing this group, appears to be essentially dependent upon the concentration.

48. "On the Existence of Polyiodides in Nitrobenzene Solution." By H. M. DAWSON and R. GAWLER.

In the course of experiments on the ratio of distribution of iodine between potassium iodide solution and nitrobenzene, it was observed that as the amount of iodine added was continually increased, the concentration of the iodine in the aqueous layer reached a maximum value and then gradually decreased.

Further distribution experiments, made with a view of explaining this peculiar phenomenon, showed that the potassium iodide in the aqueous solution was extracted by the nitrobenzene on addition of iodine to the system. Using the same volumes of nitrobenzene and potassium iodide solution in successive experiments, the amount of potassium iodide thus extracted by addition of varying quantities of iodine was determined, and further, the influence of the amount of nitrobenzene for constant quantities of potassium iodide solution and of iodine was investigated. The removal of the potassium iodide by the nitrobenzene is probably due to the formation of polyiodides and the great solubility of the latter in nitrobenzene.

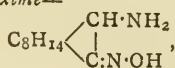
With a view of determining the nature of the polyiodides thus formed, the solubility of potassium iodide in nitrobenzene containing different quantities of iodine has been determined. If the concentration of the iodine does not exceed 0.3 grm.-molecules per litre, it is found that one molecule of potassium iodide dissolves for each molecule of iodine present, indicating the formation of the triiodide. As the concentration of the solutions thus saturated with regard to potassium iodide increases, the molecular ratio of iodine to potassium iodide gradually increases and approximates to the value two.

Determinations have also been made of the solubility of iodine in nitrobenzene containing potassium iodide. For all solutions containing more than sixty grms. of potassium iodide per litre, the molecular ratio of the dissolved iodine to potassium iodide is equal to four, and there is some probability that this ratio holds for the more dilute solutions if the uncombined iodine present in the solution is taken into account. The results of this series of solubility determinations lead to the conclusion that the polyiodide KI_5 is present in the solution.

The nitrobenzene solutions have been examined with regard to their electrical conductivity, and in accordance with the high dielectric constant of nitrobenzene it is found that the solutions are good conductors. Their conductivity is approximately one-fifth that of aqueous solutions of potassium iodide of the same molecular concentration. Determinations of the freezing point of solutions of iodine in nitrobenzene, and of solutions containing in addition to iodine an equimolecular amount of potassium iodide, indicate that the triiodide is dissociated to a very considerable extent, although the difficulties of freezing point measurements with nitrobenzene as solvent prevent an accurate quantitative estimation of the degree of dissociation.

49. "Derivatives of α -Aminocamphoroxime." By A. LEPWORTH and A. W. HARVEY.

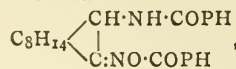
α -Aminocamphoroxime—



is made by heating aminocamphor with a solution of hydroxylamine acetate in presence of a large excess of sodium acetate. It crystallises from benzene in flattened prisms or thin plates melting at $144-145^\circ$ and dissolves in dilute alkalis and acids. It has $[\alpha]_D = +60.5^\circ$ in a 1 per cent solution in absolute alcohol and $+36.7^\circ$ in dilute acids.

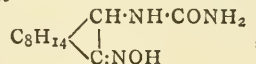
The hydrochloride, $C_{10}H_{18}N_2O_3 \cdot HCl \cdot H_2O$, forms small prisms and has $[\alpha]_D = +38.3^\circ$ in water. The platinum-chloride, $(C_{10}H_{18}N_2O)_2PtCl_6$, forms yellow needles melting and decomposing at $209-211^\circ$.

The dibenzoyl derivative—



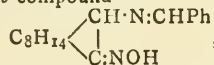
crystallises in brilliant prisms which melt at $146-147^\circ$. In absolute alcohol $[\alpha]_D = +104.8^\circ$.

The carbamide—



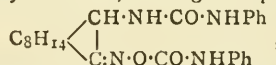
crystallises in two forms, which appear, however, to melt and decompose at the same temperature, namely, $203-204^\circ$. It has $[\alpha]_D = +40.9^\circ$ in absolute alcohol.

The benzylidene compound—



prepared by the interaction of the oxime with benzaldehyde in alcoholic solution, forms brilliant, transparent, apparently hemimorphic prisms melting at $153-154^\circ$. In alcohol $[\alpha]_D = 226.9^\circ$.

Aminocamphoroxime unites with two molecular proportions of phenylcarbimide, forming a compound—



which crystallises in asbestos-like needles melting at $175-177^\circ$. In absolute alcohol $[\alpha]_D = -56.6^\circ$.

The products obtained by the action of heat or of dehydrating agents, such as acetyl chloride, upon aminocamphoroxime do not appear to contain any compound corresponding with the camphenonitriles.

50. "Preparation of Sulphamide from Ammonium Amidosulphite." By E. DIVERS and M. OGAWA.

It has been pointed out by the authors (*Trans.*, 1900, lxxvii., 324) that a substance, apparently sulphamide, is one of the products of decomposition of ammonium amidosulphite. They have since proved that this substance is sulphamide, and that ammonium amidosulphite is a much better source of it than sulphuryl chloride has been found to be by Hantzsch and Holl (*Ber.*, 1901, xxiv., 30). The yield is 10 per cent or more, and it is accompanied by no substances which are difficult to remove. Ammonium amidosulphite is slowly heated to, and then maintained at, a temperature of about 70° , so as first to decompose the salt and then to destroy much of the thionic compounds which accompany the sulphamide. The product is dissolved in water and practically everything but ammonium amidosulphate separated from the sulphamide by treating the solution with barium hydroxide and with silver nitrate. With some simple precautions, necessitated by the presence of the amidosulphate, the sulphamide is precipitated as silver salt and recovered from this, almost as Traube directs.

51. "Hypoiodous Acid." By R. L. TAYLOR.

It has been concluded by Orton and Blackman (*Trans.*, 1900, lxxv., 830) that "the solutions obtained from iodine and mercuric oxide contain only a small quantity of hypoiodite, and that the iodine is chiefly present as iodate." This is contrary to the results described by the author in a former paper (*Mem. Manchester Phil. Soc.*, 1897, xli., 8), where he used aqueous iodine (1 part in 5000), and obtained 80 to 90 per cent of the possible amount of hypoiodite. He has made further experiments and finds that the proportion of iodine existing in the filtrate as hypoiodous acid increases with the fineness of division of the iodine, and diminishes as the proportion of iodine to the water employed increases, and with the time occupied in shaking and filtering. Using powdered

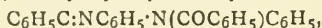
iodine, about 2 parts to 1000 of water, and occupying (as Orton and Blackman did) fifteen minutes in shaking and ten minutes in filtering, the author obtains results not very different from theirs; but using precipitated iodine with the same proportion of water, and taking only a little over a minute in shaking and filtering, the filtered liquid contains 44 to 52 per cent of the possible amount of iodine as hypiodous acid, and of the total iodine in the filtered liquid 90 to 95 per cent exists as hypiodous acid, and only 5 to 10 per cent as iodic acid. The solution of hypiodous acid decomposes very rapidly, beginning to turn brown, owing to the liberation of iodine, almost immediately after filtering, unless a very dilute solution of iodine has been employed. Consequently, it is impossible to obtain good results unless all the operations are performed very quickly. The filtered liquid always contains a little mercury. The author has estimated this, and finds that although the hypiodite in the filtrate may exist partly as mercuric hypiodite, there is so little mercury present that a considerable proportion of the iodine must exist as hypiodous acid.

52. "Synthesis of Imino-ethers. N-aryl Benziminoethers." By G. D. LANDER.

The preparation of imino-ethers of the type $\text{Ph}\cdot\text{COR}:\text{NPh}$ from the imide chlorides of the corresponding benzoyl arylamines was described. The reaction between the imide chlorides and sodium alcoholates occurs most readily when the latter are employed in alcoholic solution. Intra-molecular re-arrangement does not take place in the formation of the methyl compounds.

N-phenylbenziminioethyl ether, $\text{C}_6\text{H}_5\text{C}(\text{OEt}):\text{NC}_6\text{H}_5$, boils at $168-170^\circ$ at 14 m.m.; the methyl compound at $157-158^\circ$ at 12 m.m., and the n-propyl ether at $177-179^\circ$ at 11 m.m.

As a by-product in the synthesis of the methyl and ethyl ethers, benzoyldiphenylbenzenyl amidine,—

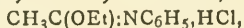


yellow prisms of m. p. $170-172^\circ$, was detected.

N-o-tolylbenziminioethyl ether, $\text{C}_6\text{H}_5\text{C}(\text{OEt}):\text{NC}_7\text{H}_7$, boils at $179-180^\circ$ at 15 m.m., the methyl ether at 173° at 15 m.m.

N-p-tolylbenziminioethyl ether boils at 178° at 11 m.m., the methyl ether at 177° at 12 m.m.

Reference was made to the formation by the action of acetyl chloride containing hydrochloric acid on a light petroleum solution of the base, of the hydrochloride of N-o-tolylacetiminioethyl ether, $\text{CH}_3\text{C}(\text{OEt}):\text{NC}_7\text{H}_7\cdot\text{HCl}$, which is crystalline, melts at $109-110^\circ$, and decomposes into ethyl chloride and acetotoluidide. Similarly, N-phenylacetiminioethyl ether hydrochloride,—



m. p. 100° with decomposition, has been prepared for the first time.

*53. "Nitration of s-Trihalogenacetanilides." By K. J. P. ORTON.

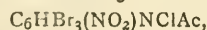
As a sequel to the author's work on the action of nitric acid on s-trihalogenanilines (*Proc.*, xviii., 58) the nitration of s-tribromoacetanilide and of 4-chloro-2:6-dibromoacetanilide has been investigated. Remmers (*Ber.*, 1874, vii., 351) and Bentley (*Amer. Chem. Journ.*, 1898, xx., 472) have subjected s-tribromoacetanilide to the action of fuming nitric acid; the former obtained an anilide, $\text{C}_6\text{HBr}_3(\text{NO}_2)\text{NHAc}$, crystallising in yellow needles from which an aniline, $\text{C}_6\text{HBr}_3(\text{NO}_2)\cdot\text{NH}_2$, was prepared by hydrolysis with ammonia; it crystallised in yellow needles, and melted at $214-215^\circ$, whilst 2:4:6-tribromo-3-nitroaniline, according to Körner (*Jahresberichte*, 1875, 347), melts at 102.5° . Bentley was unable to confirm Remmer's results.

By cautiously warming the anilides above mentioned with fuming nitric acid, the author has obtained respectively 2:4:6-tribromo-3-nitroacetanilide and 4-chloro-2:6-dibromo-3-nitroacetanilide. In neither case was the nitration complete; the nitrated anilide was isolated in a

pure state by conversion of the mixture of anilides into the acetyl-chloroamino-derivatives; the latter can be readily separated by fractional crystallisation from petroleum, in which the nitrated chloroamine (for example, acetyl-chloroamino-2:4:6-tribromo-3-nitrobenzene) is but little soluble. By treatment with alcohol, the anilide is obtained from the pure acetylchloroamino-derivative.

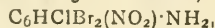
The following substances have been prepared:—

2:4:6 Tribromo-3-nitroacetanilide, $\text{C}_6\text{HBr}_3(\text{NO}_2)\text{NHAc}$, from 2:4:6 tribromo-3-nitroaniline (m. p. 102° , Körner), and by nitrating s-tribromoacetanilide, colourless needles, m. p. $216-217^\circ$; 2:4:6-tribromo-3-nitroacetanilide, $\text{C}_6\text{HBr}_3(\text{NO}_2)\cdot\text{NHAc}$, rhombs, m. p. $175-176^\circ$; acetyl-chloroamino 2:4:6-tribromo-3-nitrobenzene,—



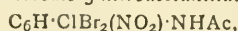
prisms, m. p. 159° .

4-Chloro-2:6-dibromo-3-nitroaniline,—



prepared by brominating 4-chloro-3-nitroaniline (m. p. 103°), and by hydrolysis of the corresponding anilide, pale yellow needles, m. p. $103-104^\circ$.

4-Chloro-2:6-dibromo-3-nitroacetanilide,—



prepared from the corresponding aniline and by nitrating 4-chloro-2:6-dibromoacetanilide, silky needles, m. p. 224° ; acetylchloroamino 4-chloro-2:6-dibromo-3-nitrobenzene, $\text{C}_6\text{HClBr}_2(\text{NO}_2)\cdot\text{NClAc}$, short prisms, m. p. $134-135^\circ$.

Attention is called to the fact that, whereas in the action of nitric acid on s-tribromoaniline a nitroamine is first formed, which then undergoes change, the nitro-group displacing the para-bromine atom in the nucleus (*Proc.*, xviii., p. 58), with the anilide no such displacement occurs, but only nitration in the meta-position. Acetylation, combined with the presence of two ortho-placed halogen atoms, prevents partially, at least, the amino group from exercising its usual directing function.

54. "Purpurogallin." Preliminary Notice. By A. G. PERKIN and A. B. STEVEN.

To purpurogallin, an oxidation product of pyrogallol, Clermont and Chautard (*Jahresbericht*, 1882, 683) assigned the formula $\text{C}_{20}\text{H}_{16}\text{O}_9$, and described a tetra-acetyl compound, $\text{C}_{20}\text{H}_{12}\text{O}_9(\text{C}_2\text{H}_5\text{O})_4$, m. p. 186° , and a tetrabromo-derivative, $\text{C}_{20}\text{H}_{12}\text{Br}_4\text{O}_9$, m. p. $202-204^\circ$. Nietzki and Steinmann (*Ber.*, 1887, xx., 1278) preferred the formula $\text{C}_{18}\text{H}_{14}\text{O}_9$, and found that on distillation with zinc dust naphthalene is produced. This preliminary investigation, while corroborating, as a rule, the analytical numbers of these chemists, indicates that the molecular weight of purpurogallin is much lower, most probably being represented by $\text{C}_{11}\text{H}_8\text{O}_5$. The tetra-acetyl compound, m. p. $182-183^\circ$, $\text{C}_{11}\text{H}_4\text{O}_5(\text{C}_2\text{H}_5\text{O})_4$, and the tribenzoyl compound, $\text{C}_{11}\text{H}_5\text{O}_5(\text{C}_7\text{H}_5\text{O})_3$, minute colourless prisms, m. p. 213° (found, C = 71.99; H = 3.86; molecular weight [cryoscopic] = 556), have been studied. Analyses of the dibromo-compound, $\text{C}_{11}\text{H}_6\text{Br}_2\text{O}_5$, m. p. $204-206^\circ$ (found, C = 35.10; H = 1.67), and the monopotassium salt, $\text{C}_{11}\text{H}_7\text{O}_5\cdot\text{K}$ (found, K = 14.76), minute brown-violet needles, point to the correctness of this formula. Hooker (*Ber.*, 1887, xx., 3260), by means of nitrous acid, obtained purpurogallin from gallic acid. If, however, potassium ferricyanide in conjunction with potassium acetate be employed, a small quantity of a new compound crystallising in minute orange-red needles is formed, which appears to be purpurogallin carboxylic acid, $\text{C}_{11}\text{H}_7\text{O}_5\cdot\text{CO}_2\text{H}$ found, C = 54.56, 54.14; H = 3.73, 3.18).

55. "Quercetagetin." By A. G. PERKIN.

Quercetagetin was isolated from the flowers of the African marigold (*Tagetes patula*) by Latour and Magnier de la Source (*Bull. Soc. Chim.*, 1877, xxviii., 337) as a yellow crystalline substance, $\text{C}_{27}\text{H}_{22}\text{O}_{13} + 4\text{H}_2\text{O}$. A re-investigation indicates that its true formula is $\text{C}_{15}\text{H}_{10}\text{O}_8$ (found, C = 56.66, 56.47; H = 3.25, 3.31), as it gives a sul-

phate, $C_{15}H_{10}O_8.H_2SO_4$ (found, $C = 43.28$; $H = 3.29$), orange needles, and a *monopotassium* salt, $C_{15}H_9O_8K$ (found, $K = 10.74$). Quercetagenin melts at $318-320^\circ$, gives an *acetyl* compound, $C_{15}H_4O_8(C_2H_3O)_6$ (found, $C = 57.37$; $H = 3.87$; $C_{15}H_{10}O_8 = 55.82$), colourless needles, m. p. $203-205^\circ$, and dyes shades browner, though somewhat similar to quercetin, to which class of colouring-matter it appears to belong. It contains no methoxyl group, and on fusion with alkali gives protocathechuic acid and a phenol at present unidentified. As there is considerable difficulty in obtaining raw material, the conclusion of the investigation may be delayed for some time.

NOTICES OF BOOKS.

The Elements of Physical Chemistry. By HARRY C. JONES, Associate Professor of Physical Chemistry in the Johns Hopkins University. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1902. Pp. 565.

WITHIN the last fifteen years a new branch of science has come into existence, occupying a position between physics and chemistry, and known as physical chemistry. The term is not new, though the new science is different to the old.

In the author's opinion it is not necessary to reject or ignore the work of such men as Gladstone, Bunsen, Koppe, and Regnault in order to appreciate the gigantic strides made by the *new* physical chemistry; it is in their work that lies the foundation of much that has been developed within the last few years.

No one can use this book successfully without an elementary knowledge of physics, chemistry, and mathematics, and it would be well to add the elements of thermodynamics and differential equations.

The new physical chemistry really begins with the chapter on solutions; the discovery of the relations between dilute solutions and gases has placed the subject of solutions at the very foundation of the new developments in physical chemistry.

Matter is known in three different states—solid, liquid, and gaseous; and as matter in every state can be mixed with matter in every other state, it is obvious that we can have nine different classes of solutions. These are—gas in gas, liquid in gas, solid in gas, gas in liquid, liquid in liquid, solid in liquid, gas in solid, liquid in solid, solid in solid; and it is stated in advance that well-defined examples of all these classes are known. In this chapter, which fills over 100 pages, the author considers solutions in all their bearings; osmotic-pressure, the relations between osmotic-pressure and gas-pressure, the theory of electrolytic dissociation, the lowering of the freezing-point of solvents by dissolved substances, diffusion, colour, and other properties of solutions.

Little or nothing was heard of solid solutions until van't Hoff published his now well-known paper about eleven years ago. When some substances are dissolved in solvents other than water they give abnormally small depressions of the freezing-point. After studying and experimenting on this subject van't Hoff was led to suspect that when certain solutions are frozen the solid which separates is not the pure solvent, but a mixture of the solvent and the dissolved substance, forming a solid solution. If a solid solution is a solid homogeneous complex of several substances, in which the properties can change without destroying the homogeneity, then examples are known, such as the alums and the formation of "mixed crystals" which are to be distinguished from double salts.

A striking example of diffusion in solids where no chemical action takes place is the penetration of hot porcelain by carbon; when a porcelain crucible is heated in graphite the carbon completely penetrates the porcelain; zinc objects covered with a thin layer of copper gradually become white; while, as Sir Wm. Roberts-Austen has

lately shown, discs of gold and lead clamped together and kept at a constant temperature of $18^\circ C.$ for four years, were found to have adhered to each other, whilst the gold had penetrated the lead to a distance of 8 millimetres.

The remainder of the book has largely to do with energy changes, as, in the author's opinion, the fundamental problems of chemistry will never be solved by a study of the material changes alone, but only through elaborate investigations of the energy relations which obtain in systems before reactions, and in the products of the reactions.

The transformations of chemical energy into heat constitute the subject-matter of Chapter VI. on thermochemistry; electrochemistry, Chapter VII., deals with the transformation of chemical energy into electrical, and *vice versa*. The relations between light and chemical energy furnish the material for Chapter VIII. on photochemistry, and the velocities with which chemical reactions take place, and the conditions of equilibrium in such reactions are examined in Chapter IX., on chemical dynamics and chemical equilibrium; while in Chapter X. measurements of the relative chemical activities of different substances are considered.

It is not too much to say that this is a valuable and important work, and gives in one volume the co-ordinated results of many separate workers. The subject of physical chemistry has already extended into nearly every field of chemical science; it has thrown light on many problems in chemistry, as well as in physics; it has also reached out into biology; and that physical chemistry is to find its way into the geological sciences has become obvious from the work of van't Hoff in the last two or three years.

An Introduction to Modern Scientific Chemistry, in the Form of Popular Lectures Suited for University Extension Students and General Readers. By Dr. LASSAR-COHN, Professor in the University of Königsberg. Translated from the Second German Edition by M. M. PATTISON MUIR, M.A. With 58 Illustrations by the Author. London: H. Grevel and Co. 1901. Pp. 348.

In this volume the author has endeavoured to give a succinct and accurate demonstration of chemistry on strictly scientific lines, and at the same time in as popular a form as is compatible with the matter and the vast range of the subject.

The form followed in lectures is used as far as possible, and experience has shown that this method adds to the interest of the subject. The book, however, is not divided into numbered chapters, but simply goes on from one subject to another with hardly a break.

The author is lucid in style, and does not overburden his work with an excess of theoretical considerations.

We must, however, remark on the eccentric nature of the illustrations, which, we read, are by the author himself. The lack of perspective in most of them is very noticeable, while throughout they are of the crudest description and are often quite unnecessary. A glance at pages 7, 15, 26, 143, or 176, to mention only a few, will enable the reader to follow our meaning. Otherwise the book is well and clearly printed, and the index is all that can be desired.

Royal Institution.—On Tuesday next, April 8th, Dr. Allan Macfadyen, of the Jenner Institute of Preventive Medicine, will deliver the first of a course of three lectures at the Royal Institution on "Biological Inquiry"; on Thursday, April 10th, Professor Dewar will begin a course of three lectures on "The Oxygen Group of Elements"; and on Saturday Dr. W. H. Cummings, Principal of the Guildhall School of Music, will commence a course of three lectures on "British National Song," with Musical Illustrations. The Friday Evening Discourse on April 11th will be delivered by Professor Dewar on "Problems of the Atmosphere"; and on April 18th by Sir John H. A. Macdonald, his subject being "The Autocar."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 10, March 10, 1902.

Preparation and Properties of a New Silicon Hydride.—H. Moissan and S. Smiles.—During the solidification of the condensation products resulting from the action of dilute hydrochloric acid on magnesium silicide by means of liquid air, the authors obtained a mixture which after fractionation yields a gas and a liquid body, the latter spontaneously inflammable in air. The gas they intend to further investigate. The liquid compound contains for one molecule of silicon a molecule and a-half of hydrogen. To this they attribute the formula Si_2H_6 , by analogy with ethane gas, and they hope to be able to verify this theory and to establish the vapour density of this new compound.

Researches on the Transformations of Steel by the Dilatometric Method.—Georges Charpy and Louis Grenet.—Using the dilatometric method, two transformations are observed in iron-carbon alloys:—(1) A sudden change taking place at 700° , with contraction of volume; this corresponds to the absorption of heat observed at the critical-point α_1 in the pyrometric method. (2) A gradual change, apparently corresponding to a contraction for steels containing more than 0.85 per cent of carbon, and to a dilatation for steels containing more than 0.85 of carbon and ending at a temperature approaching that of the critical-point α_3 , as indicated by the pyrometric method. The critical-point α_2 , which is observed towards 750° by the pyrometric method, apparently corresponds to no variation in the phenomenon of dilatation.

Action of Hydrogen Peroxide on Zinc Oxide.—M. de Forcrand.—The author's researches on the peroxidation of zinc oxide by means of peroxide of hydrogen lead him to the following results:—(1) There exists no oxide of zinc intermediate between ZnO and Zn_3O_5 , and consequently the products obtained by Thénard and Kouriloff are mixtures. The same is also true of Haass's oxide, Zn_3O_8 . (2) There exist three different degrees of peroxidation of zinc, Zn_3O_5 , Zn_4O_7 , and ZnO_2 ; the first is stable at 100° , the last is extremely unstable, even in the cold. (3) These bodies are all hydrated, and permanently retain at least as many molecules of water as atoms of oxygen in excess, in such a manner that they may just as well be considered as compounds of hydrogen peroxide and the protoxide (anhydrous or hydrated) as hydrated peroxides.

A New Sodium Phosphate.—H. Joulie.—The author shows that there exists a phosphate of sodium intermediate between monosodic and disodic phosphates which might be called the sesqui-sodic phosphate, and which corresponds to the formula $3\text{NaO}_3\text{HIO}_2\text{PO}_5$. This phosphate differs from disodic phosphate (1) in being much more soluble in water and much more easily preserved in the form of a concentrated solution without crystallising; (2) in medicine it is active in much smaller doses; (3) it has a slight and not unpleasant taste; (4) it will probably be able to be employed for hypodermic injections in more concentrated solutions than disodic phosphate.

Reduction of the Ortho-nitrated Azoic Colouring-matters. Production of Substituted Derivatives of Phenyl-pseudo-azimidobenzol.—A. Rosenstiehl and E. Suais.—When azoic colouring-matters derived from para- and meta-nitramines are reduced, it is possible to obtain the nitramines, azoxyamines, and the corresponding free azoamines or the azoic colouring-matters derived from the azoxyamines or phenylenediamines, ac-

cording to the nature of the reducing agent employed. The reactions are often quantitative. With azoic colouring-matters derived from orthonitramines a different reaction takes place. According as the reducing agent is an alkaline solution of glucose or of a sulphide, a single product is obtained less sensitive to an excess of the reducing agent. The reaction is general; the authors establish it for orthonitraniline and the isomeric ortho-nitrotoluidines.

Variation in Rotatory Power of Stable Left-hand Ether Salts of Borneol.—J. Minguin and E. Grégoire de Bollemont.—The authors examine the influence of the substitution of certain radicles for the hydrogen atom of OH. For this purpose they prepare from the stable left-hand isomer (borneol $[\alpha]_D = -38.09^\circ$) a series of ether salts. Their properties with regard to rotatory power, boiling-point, &c., are given in a table.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxv., No. 15.

Active Erythrites.—L. Maquenne and G. Bertrand.—Already noticed.

Racemic Erythrite.—L. Maquenne and G. Bertrand.—Already noticed.

Some New Derivatives of Dialcoylamidobenzoylbenzoic and Tetrachlorised Dialcoylamido-m-oxylbenzoic Acids. The Dialcoylamidised Anthraquinones and the corresponding Dialcoylamidised Oxyanthraquinone.—MM. Haller and Umbgrove.—The authors have already given the preparation of the tetrachlorised dimethyl- and diethylamidobenzoylbenzoic acids, as well as that of a certain number of their ethers and their mixed anhydrides. By reacting with nascent nitrous acid, or nitric acid, on the dimethylamidised acid, they have obtained the nitroso and nitrated derivatives.

The Synthesis of Hexamethyltriimidodiphenylene-phenylmethane and of the Colouring Material derived from it.—A. Haller and A. Guyot.—Already noticed.

On Hydrochlorate of Urea from Phenylhydrazine.—P. Cazeneuve.—In a paper on the acid molecular compounds of urea from phenylhydrazine (diphenylcarbazine), the author described a series of combinations with the organic acids, but he was unable to obtain the hydrochloric compound of this body any more than the nitric or sulphuric compounds. However, the hydrochloric compound can be obtained under the following conditions:—Five grms. of urea are dissolved in 60 to 80 c.c. of hot alcohol at 93° . Into this alcoholic solution, when nearly cold, a large excess of anhydrous ether saturated with hydrochloric acid gas is poured. Gradually the hydrochlorate of urea crystallises out in small crystals having the appearance of cauliflowers. This body is white and insoluble in water or ether, but soluble in hot alcohol. It deteriorates in boiling water. It is not decomposed *in vacuo* over soda-lime, and melts with decomposition at 125° . The estimation of the hydrochloric acid, carried out with a titrated solution of soda on the substance dried *in vacuo*, gave the following results:—Substance taken, 0.595 gm.; HCl = 0.07738 gm., or 12.97 per cent Cl. The formula $\text{CO} \begin{smallmatrix} \text{NH.NH.C}_6\text{H}_5 \\ \text{NH.NH.C}_6\text{H}_5 \end{smallmatrix} \text{HCl}$ requires 12.94 per cent. Ordinary urea also gives a mono-hydrochloric compound.

The Chromised Violet Colouring-matters derived from Diphenylcarbazine.—P. Cazeneuve.—The compound specially dealt with in this paper was prepared in the following manner:—Twelve grms. of urea from phenylhydrazine were dissolved in 25 grms. of hot acetic acid and 25 grms. of water. Chromic acid in equimolecular proportion was gradually added; that is, 5 grms. dissolved in 50 grms. of water. Carbonic acid is given off, and at the same time the liquid takes a deep violet tint. On cooling, most of the colouring material is deposited.

The supernatant liquid is decanted. The residue is taken up with hot alcohol, and the colouring material is again deposited on cooling. This is repeated several times. The author then goes on to describe the various properties and reactions of this body. Another similar colouring matter was obtained by using a much smaller quantity of chromic acid; the resulting body contains only 0.93 per cent of chromium, against 5.62 or 5.5 in the former one. These two materials, however, possess the same properties with regard to dyeing.

The Use of Diphenylcarbazine for the Detection of Chromic Acid in Cotton Dyed with Chrome Yellow.—P. Cazeneuve.—Diphenylcarbazine is the most delicate reagent for chromic acid, without the possibility of confusion with any other metallic body; its sensitiveness reaches even more than 1 part in 1,000,000. Any chromate in aqueous solution, slightly acidulated with acetic or hydrochloric acid, gives an intense violet colouration with diphenylcarbazine in the form of powder. For testing cotton goods, the material is placed in a test-tube with 1 c.c. of a $\frac{1}{10}$ th per cent solution of potash. The threads are instantly bleached in the case of chromate of lead or chrome yellow. The liquid is then made strongly acid with acetic acid. A few grains of diphenylcarbazine or of acetate of diphenylcarbazine added to the liquid develop, on agitation in the cold, a beautiful violet colouration. This reaction is trustworthy, sensitive, and rapid.

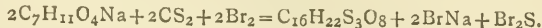
Characteristics of Essences of Orange Flowers from the 1901 Crop.—Eug. Theulier.—The author gives, in the form of a table, a number of physical constants, proportions of ethers, and anthranilate of methyl observed in a large number of samples taken from the daily distillations from May 16 to June 2, 1901.

MISCELLANEOUS.

Oxidation by the Oxygen of the Air.—H. Biltz.—The slow oxidations brought about by the oxygen of the air, in the presence of water, are accompanied by a secondary formation of peroxide of hydrogen. Examples of this action, first observed by Schoenbein, are not yet very numerous in organic chemistry; the oxidation of the phenylhydrazone of dibromo-*p*-oxybenzaldehyde is, however, a very good example. Two grms. of the phenylhydrazone are dissolved with 3 grms. of potassic hydrate in 50 grms. of alcohol and 30 c.c. of water. A current of air is passed through the solution; after four hours the dilute solution, slightly acidulated with hydrochloric acid, is treated with a large excess of acetate of soda. The osazone thus precipitated is a crystalline powder, soluble in alcohol, fusible at 206°, and having the formula $C_{26}H_{20}N_4Br_4O_2$. In the mother-liquors from the precipitation, diluted to 1 litre, the peroxide of hydrogen can be detected by all the usual reagents; it can be titrated without difficulty with permanganate of potash or iodide of potassium. It can be seen thus that the oxygen of the osazone and that of the peroxide of hydrogen are equal in weight. If, on the other hand, we estimate the amount of oxygen contained in the air used, we find that it is equal to the sum of the oxygen of the osazone, and that of the peroxide of hydrogen together. The oxidation is therefore expressed by the following equation:— $2C_{13}H_{11}N_2Br_2O + O_2 = C_{26}H_{20}N_4Br_4O_2 + H_2O_2$.—*Berichte*, vol. xxxiii., p. 2295.

Action of Bromine and Sulphide of Carbon on the Methylenic Soda Compounds.—G. Wenzel.—It is well known that iodine transforms soda malonic ether into acetylenetetracarbonic ether by the separation of iodide of sodium and the junction of the two remaining portions of malonic ether. Bromine, in sulphocarbonic solution, reacts differently on this same body. Bromide of sodium is formed, as well as bromide of sulphur, and a compound

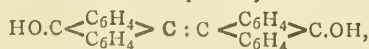
which crystallises in yellow needles fusible at 139° and having the formula $C_{16}H_{22}S_3O_8$:—



The return from the operation is only from 5 to 20 per cent of theory. This body is soluble in alcohol, insoluble in soda, and hardly attacked by acids in the cold. Soda cyanacetic ether undergoes an analogous transformation under the same influences. We obtain a compound, fusible at 225°, of the formula $C_{12}H_{22}N_2S_3O_4$, insoluble in water and ligroin, but soluble in alcohol. The soda compounds of acetylacetone, and of the acetic and phenylacetic ethers will be examined from the same point of view.—*Berichte*, vol. xxxiii., p. 2041.

Action of Fuming Nitric Acid on the Substituted Acrylic Acids.—A. Wahl.—The author has reacted with fuming nitric acid on the crotonate, tiglate, and isolauro-nolate of ethyl, and on cinnamate of methyl. He describes the methods adopted and the reactions obtained.—*Bull. Soc. Chim.*, Series 3, xxv., No. 16—17.

The Action of Nitric Acid on Anthracene.—O. Dimroth.—The author has elaborated a method of nitration of anthracene which has given him good results. Fifty grms. of finely powdered anthracene are suspended in 200 c.c. of acetic acid, and 20 c.c. of nitric acid at 63 per cent are then added without allowing the temperature to go above 30–35°. The anthracene is dissolved, and the solution very probably contains nitroacetate of anthracene, which, when heated with dilute soda-lye, is transformed into nitroanthracene. If we add fuming hydrochloric acid and acetic acid to the above nitric and acetic solution, while still keeping the temperature down, we obtain chloride of nitroanthracene $C_{14}H_{10}(NO_2)Cl$, which, when digested with dilute soda-lye, also gives nitroanthracene. This compound can be obtained perfectly pure, in yellow prisms fusible at 149°, by a single crystallisation in acetic acid. The above-mentioned chloride occurs in needles fusible at about 163°; if the nitric solution is heated, first on the water-bath and then to boiling, nitric oxide is given off, and a substance deprived of nitrogen is formed which is probably a dianthranol—

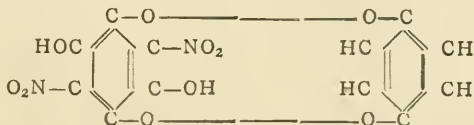


or rather a dianthrone—



This compound is identical with the product obtained in different manners by Orndorff and Bliss, starting with anthranol.—*Berichte*, vol. xxxiv., p. 219.

Action of Nitrous Acid on Quinone.—J. Schmidt.—By passing nitrous acid fumes produced by the attack of As_2O_3 with HNO_3 through an ethereal solution of quinone (10 grs. per 250 c.c.) and cooling to about 78°, a crystalline deposit of *nitranilic-quinone* is obtained—



This new compound crystallises in brilliant yellow prisms having an odour of quinone; it decomposes at about 100–160°, is soluble in water, alcohol, and ether, and slightly soluble in benzene and chloroform. Alkalis decompose it into alkaline nitranilate and quinone by the splitting up of the molecule. Fifteen grms. of liquid nitrous acid placed in a sealed tube with 3 grms. of quinone, reacted violently after twelve hours' contact; the explosion blew the wrought-iron tube enveloping the sealed glass tube into fragments, and these penetrated the walls and doors of the laboratory to a depth of several centimetres.—*Berichte*, vol. xxxiii., p. 3246.

MEETINGS FOR THE WEEK.

- MONDAY, 7th.—Royal Institution, 5. General Monthly Meeting.
— Society of Chemical Industry, 8. "Some Recent Improvements in the Photography of Colour" (Illustrated by Lantern Slides), by E. Sanger Shepherd.
- TUESDAY, 8th.—Royal Institution, 3. "Recent Methods and Results in Biological Inquiry," by Allen Macfadyen, M.D., B.Sc., Fullerian Professor of Physiology, R.I.
— Society of Arts, 8. "Street Architecture," by Prof. Beresford Pite, F.R.I.B.A.
- WEDNESDAY, 9th.—Society of Arts, 8. "Ceuta and Gibraltar," by Major-Gen. John F. Crease, C.B.
- THURSDAY, 10th.—Royal Institution, 3. "The Oxygen Group of Elements," by Prof. Dewar, M.A., LL.D., D.Sc., F.R.S., Fullerian Professor of Chemistry, R.I.
- FRIDAY, 11th.—Royal Institution, 9. "Problems of the Atmosphere," by Prof. Dewar, M.A., LL.D., D.Sc., F.R.S., &c.
— Physical, 5. "An Apparatus for Vapor-pressure Measurements," by Mr. Grant. "The Use of Cathode Rays for Alternating Current Measurements" and "An Experiment on the Current Growth in an Inductive Circuit," by Mr. Morris. "An Electric Heater," by Dr. R. A. Lehfeldt. "Note on the Compound Pendulum," by S. A. F. White.
- SATURDAY, 12th.—Royal Institution, 3. "British National Song" (with Musical Illustrations), by William H. Cummings, Mus.D. (Dub.), F.S.A., Hon R.A.M., Principal of the Guildhall School of Music.

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Experimental Physics Prof. W. FRESENIUS, Ph.D.
Stoichiometry Prof. W. FRESENIUS, Ph.D.
Organic Chemistry L. GRÜNHUT, Ph.D.
Chemical Technology W. LENZ, Ph.D.
Microscopy, with exercises in Microscopic work Prof. H. FRESENIUS, Ph.D.
Chemistry and Analysis of Foods Prof. W. FRESENIUS, Ph.D.
and Prof. E. HINTZ, Ph.D.
Hygiene Dr. med. G. FRANK.
Practical exercises in Bacteriology J. HUBER.
Technical Drawing, with exercises J. HUBER.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL's Verlag, at Wiesbaden, or to one of the Directors.

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ALFRED JØRGENSEN, The Laboratory, Copenhagen, V

THE CHEMICAL NEWS.

VOL. LXXXV., No. 2211.

ON THE RADIO-ACTIVITY OF MATTER.*

By HENRI BECQUEREL, D.C.L., Ph.D.,
Member of the Academy of Sciences, Paris.

THE property possessed by certain bodies of emitting invisible and penetrating rays was unknown six years ago. The speculations brought about by the experiments of M. Röntgen led to the examination of material bodies, to see if any of them had the power of emitting similar radiations; the phenomenon of phosphorescence naturally was first thought of, being a known method for the transformation and emission of energy. This idea, however, could not be applied to the phenomena with which we are occupied, but it was very fruitful. It led to the choice, among phosphorescent bodies, of the salts of uranium of which the optical constitution is remarkable on account of the harmonic series of the bands of their absorption and phosphorescent spectra. It was while experimenting with these bodies in 1896 that I first observed the new phenomena which I am about to bring before you this evening. I have here the plates of the double sulphate of uranium and potassium, obtained by Lipmann's method, which I used for my first experiments. After having placed one of these plates on the black paper which covered a photographic plate, and leaving it for several hours, I observed on developing the plate that the uranium salt had emitted certain active rays, traversing the black paper, as well as various screens interposed between the plate and the active body, such as thin sheets of glass, aluminium, copper, &c. I soon saw that this phenomenon had nothing to do with phosphorescence, or with any known method of excitation, such as luminous or electric rays, or any appreciable variation of temperature.

I had to deal, therefore, with a spontaneous phenomenon of a new order. The absence of any known exciting cause on a body prepared in the laboratory several years ago, caused me to think that the phenomenon would have been the same at any time it might have been observed; it should therefore be permanent, that is to say, there should not be any appreciable weakening after a very long time. This is, in fact, what I have proved during the past six years. I will show you the first proof I had of the spontaneity of the rays; these rays have traversed the black paper which covered the photographic plate, and a thin strip of copper in the form of a cross. Here again is the radiograph, made about the same time, of an aluminium medal; the unequal absorption of the different thicknesses has caused the appearance of the effigy thereon. After the very first observation I observed that the new radiations would discharge electrified bodies, at some distance in the air, a phenomenon which gives us a second method for studying these rays; the photographic method is specially qualitative, while the electrometer furnishes numerical elements of comparison.

In the course of these first observations, I was led away from the path towards which later experiments brought me back by several facts, of which the following is the principal:—Having protected a photographic plate by means of a sheet of aluminium 2 m.m. in thickness, and having arranged on the aluminium several samples of phosphorescent powders, placed on separate plates of glass, and covered with small tubes like clock shades, the photographic proofs, obtained after forty-eight hours, showed silhouettes of the plates of glass just

as if they had been produced by the total refraction and reflection of rays identical with those of light, but which must have traversed the 2 m.m. of aluminium. This photograph is unique; I have never been able to reproduce it or obtain any action with the same sample of sulphide of calcium, nor with any other phosphorescent preparation. At about the same time M. Niewenglowski obtained an impression with sulphide of calcium, and M. Troost with hexagonal blende. To this day I do not know the cause of the activity of these products or its disappearance. These facts, and some others, gave me the idea that the new rays might be a transversal movement of the ether analogous to that of light; but the absence of refraction and a large number of other experiments made me abandon this hypothesis.

In this same year, 1896, I found that all the uranium salts emitted rays of a similar nature, that the radiant property is an atomic one belonging to the element uranium, and electric measurements showed me that metallic uranium was about three and a-half times more active in ionising air than is the double sulphate of uranium and potassium. The same method enables us to study the rôle played by the gases in the discharge, and to observe that a sphere of electrified uranium retains its charge *in vacuo*, while in air it loses it. The rate of the fall of potential is sensibly proportional to the potential if the latter is only a few volts; it should be constant and independent of the potential when this is very high. Gas rendered conducting by these rays retains this property for some instants. Between two conductors maintained at constant potentials these rays set up in air a continuous current.

These experiments were taken up and elaborated by Lord Kelvin in 1897, then by Messrs. Beattie and S. de Smolan. In 1899 Mr. Rutherford showed how the phenomena due to the conductivity communicated to gases by uranium, and the existence of a maximum in the current produced, could be explained by the hypothesis of ionisation, to which the beautiful work of Mr. J. J. Thomson has given the seal of authority.

In 1898 M. Schmidt and Mdma. Curie observed, quite independently, that thorium has properties analogous to those of uranium, properties which were specially examined by Mr. Owens and Mr. Rutherford. Mdma. Curie having measured the ionising activity of a large number of minerals containing uranium or thorium, announced the remarkable fact that several minerals were more active than metallic uranium. M. and Mdma. Curie concluded that there must be a more active body than uranium in the mineral, and they undertook the task of isolating it.

By treating one of the most active of these minerals, viz., pitchblende from Joachimstal, they first separated an active bismuth, to which they gave the name of polonium, then shortly afterwards they obtained a very active barium containing a new element, radium.

These bodies are prepared by fractional precipitations, in which one is guided by the indications of the electrometer; the activity of these products is 100,000 times greater than that of uranium.

About the same time M. Giesel succeeded in preparing some very active substances, and in 1900 M. Debierne announced the existence of a new element, actinium, about which, however, we have not heard many particulars. Of all these new bodies radium alone is characterised as a new element; it has an emission spectrum consisting of lines which do not belong to any other known body, and the atomic weight of the active salts of barium was found to increase with the proportion of radium present.

The activity of uranium was not sufficient to excite phosphorescence in other bodies; M. and Mdma. Curie, however, observed this phenomenon with the rays from radium, and further, that the salts of radium were themselves luminous, their luminosity being, like their radio-activity, spontaneous. The activity of radium produces various chemical reactions; it colours glass, it transforms

* A Discourse delivered before the Members of the Royal Institution, Friday, March 7, 1902.

oxygen into ozone, it changes white phosphorus to red, it ionises not only gases but also liquids, such as petroleum and liquid air, and insulating solid bodies, such as paraffin, developing in this latter body a residual conductivity which lasts a long time after the rays have ceased to act. It also causes on organic tissues serious burns analogous to those produced by X rays.

The sample of radium that M. and Mme. Curie have lent me for the purpose of this lecture enables me to show you a few of these phenomena—ionisation of the air, luminosity, and phosphorescence.

I have observed by means of the photograph I now show, that the radio-activity of polonium will not traverse a thin sheet of black paper forming a small cylinder closed by aluminium or mica, and at the bottom of which was placed the powdered material; the rays from radium easily pass through this envelope; we shall see that still more profound differences exist between these two kinds of rays.

The radio-activity of radium restores to certain crystals, and to glass, the property of becoming phosphorescent by heat, which they have lost owing to a previous elevation of temperature.

The phenomena of absorption, examined either by means of photography, by phosphorescence, or by ionisation of the air, showed the heterogeneity of the class of radiations emitted; subsequent observations have enlarged the field of this research.

Towards the end of the year 1899 M. Giesel, and then MM. Meyer and Schweidler, observed that the rays of radio-active preparations were deviated by a magnetic field in the same manner as are the cathodic rays. For my part, at about the same time, without having heard of these experiments, I observed the same phenomenon with radium. The experiment can be made in the following manner:—A small paper cylinder containing a few grains of the radio-active body is placed horizontally on a photographic plate covered with black paper, between the poles of a magnet; the rays are thrown entirely to one side of the plate. I here show my two first photographs, one of which shows a concentration on one pole of the magnet.

Very shortly afterwards I observed that the rays from polonium are not deviated, and consequently that two kinds of rays exist, one deviable and the other non-deviable. M. and Mme. Curie have made an electric examination of this subject which has proved the simultaneous existence of these two kinds of rays in the radio-activity of radium, their unequal permeability varying with the distance from the absorbing screens. The accompanying photograph shows these two kinds of rays from radium; I have recently observed that uranium emits only deviable rays, that is, saving the existence of much less active, non-deviable rays. In fact, there does exist a third kind of ray which are not deviable, but are extremely penetrating; they have been shown more particularly by M. Villard.

Thus the activity of radio-active bodies comprises three kinds of rays—rays which are deviable in a magnetic field, which appear to be identical with cathodic rays, and two sorts of non-deviable rays, one kind being very easily absorbed, the other resembling X rays and being very penetrating. Uranium emits principally the first kind, polonium gives only the second, and radium gives all three at once.

Let us now return to deviable rays; the material theory of Sir William Crookes and Mr. J. J. Thomson can be applied to them, and the consequences can be verified with the greatest facility. In a uniform magnetic field the trajectories perpendicular to the field are circumferential to the path ρ which leads the rays to the point of emission. For an oblique emission making an angle with the field, the trajectories are helices enveloping the cylinders with rays $\rho \sin \alpha$. By placing on a horizontal photographic plate parallel to the uniform field, a small lead box containing a few grains of radiferous barium forming a source of very small diameter, the rays are

drawn down to the plate, and excite it on one side alone; a bundle of simple rays emitted in the plane normal to the plate and parallel to the field should show theoretically an arc of an ellipse of which the axes are in the proportion of 2 and π . The accompanying photograph shows these theoretical arcs, obtained by reversing the direction of the field, the one in air and the other *in vacuo*, on a photographic plate enveloped in black paper; the intensity of the magnetic field was about 4000 C.G.S. units.

If we do not enclose the photographic plate, and if we arrange on it several strips of paper or of metal to form screens, we observe in the print of the radio-activity dispersed by the magnetic field, a species of absorption spectra. Each trajectory has a different curvature corresponding to rays of different speeds and having different penetrating powers.

Here is an example of one of these prints, obtained in a field of about 1740 C.G.S. units; the screens are a strip of black paper, a strip of aluminium of 0.1 m.m. thickness, and a strip of platinum of 0.03 m.m. thickness. To obtain a pure spectrum so that at each point of the plate a bundle of rays are found, of which the trajectories have all the same curvature, the rays should be made to issue from the source so as to pass through a small round opening; the result is the same as the preceding one. This latter also shows a very intense impression, due to the secondary rays, provoked by the rays which were stopped by the lead cover over the active body, and in which was made a small opening through which the pure spectrum passed. The absorption varies with the distance of the screen from the active body, and the rays which are stopped by a screen placed on the plate are able to traverse this same screen when it is interposed at a point near their source.

These experiments leave little doubt as to the identity of the deviable rays with cathodic rays. However, it was necessary to prove that they carry charges of negative electricity, and that they are deviated by an electric field.

M. and Mme. Curie, in a beautiful experiment, have shown that the rays of radium charge negatively the bodies that receive them, and that the source becomes charged positively. For this double experiment it is necessary that all the conductors and the source itself be completely enveloped in an insulating material, such as paraffin. For the active body examined the charge was $4 \cdot 10^{-18}$ C.G.S. units per square centimetre of radiating surface per second.

For my part, I have shown and measured the electrostatic deviation by projecting the deviated shadow of a screen placed perpendicular to the field, on a photographic plate. One of these apparatus is here shown, as well as one of the prints obtained in which on the two halves of the same plate appear the two deviated shadows corresponding to the reversal of the electric field, of which the intensity was $1 \cdot 02 \cdot 10^{12}$.

The ballistic hypothesis attributes these phenomena to material masses transporting charges of negative electricity with very great rapidity. Let m be the material mass of a particle, e its charge, and v its velocity. We know that in a magnetic field of an intensity H , the radius of curvature ρ of the circular trajectory is given by the equation

$$H \rho = \frac{m}{e} v. \text{ The numerical value of the product } H \rho$$

serves to show the character of each simple ray. On the other hand, in an electric field of an intensity F , the parameter of the parabolic trajectory is $\frac{m}{e} \frac{v^2}{F}$. The know-

ledge of these two values gives $\frac{m}{e}$ and v . With a value of $H \rho = 1600$ I obtained approximately $v = 1.6 \cdot 10^{10}$, and $\frac{m}{e} = 10^7$. These figures are entirely of the same

order in value as those which led to the measurements made with cathodic rays, and the theoretical considerations with regard to Zeeman's experiment.

From the above figures we deduce that, from the fact of the deviable radio-activity under consideration, there escapes from each square centimetre of radio-active surface 1·2 m.grms. of matter in a thousand million years.

By extending these measurements to radiations of different and well-known natures, we ought to be able to determine if the relation $\frac{e}{m}$ is constant, or variable with

one ray or another, and whether these do not differ only in their speeds; I have not yet finished the experiments I undertook to decide this fundamental question, but recently M. Kaufmann has attempted to elucidate the matter. He combined, at right angles, the magnetic and the electric actions; unfortunately, the experiment, which is very difficult to perform, did not give him one plate fit to measure. For the values of $H\rho$ comprised between 1800 and 4600, he found that the relation $\frac{e}{m}$ varied from $1\cdot3 \cdot 10^7$ to $0\cdot6 \cdot 10^7$, and the speed v from $2\cdot3 \cdot 10^{10}$ to $2\cdot8 \cdot 10^{10}$.

The proof of a regular variation in the calculated relation $\frac{e}{m}$ is of considerable theoretical importance; if

this relation was constant, as it seemed to be as the result of a large number of measurements, we might conclude that the slightly deviable rays, for which $H\rho$ is more than 5000, have speeds considerably greater than that of light.

On the other hand, theoretical considerations have given the idea that the speed could not surpass that of the propagation of electro-magnetic disturbances, that is to say, the speed of light, and we have been led to consider the mobile masses in a magnetic field as endowed with a particular inertia which is a function of the speed. Under these conditions the calculated mass ought to be apparent, or at least partly so, and it should increase indefinitely as the actual speed approaches that of light. The figures published by M. Kaufmann bear out this hypothesis.

Another consequence of this manner of looking at the question would be that there should be continuity between the deviable rays and those which are not, as the radius of curvature of the trajectories becomes infinite at the same time as the apparent mass.

The photographic print already mentioned, as well as one of the following ones, showed, on the contrary, a very distinct discontinuity, although in the second one the exposure was sufficiently prolonged for the impression of the least active rays, such as the penetrating non-deviable ones, to be distinctly visible.

This proof was obtained in the following manner:—In the uniform magnetic field of a permanent magnet, I placed, normally to the field, a photographic plate, then on this latter I arranged screens of lead fixed on a sheet of glass. These screens are pierced with openings normal to the plate, and destined to limit the width of the beam; in the path of these beams I arranged other screens, such as aluminium ones. Below the plate opposite a narrow slit in a strip of lead a small block of lead is placed having a deep cavity normal to the plate, and in which the radiant body is placed. We have thus a narrow, linear source normal to the plate and several millimetres in length. The cavity is covered with a thin sheet of aluminium to stop the light rays.

The figure represents a section made normally to the field of the beam, of which a part is deviated. Each beam corresponding to a determined speed gives an impression which is noticeably curved, as if the entire trajectory was marked on the plate. In these photographs the interior of the cylinders forming the screens is strongly affected by the secondary emission from the lead. The first picture shows that through each opening there passes an infinity of rays, constituting portions of the pure spectra. These meet with a strip of aluminium 0·1 m.m. in thickness, and traverse it without deviation, but not all with equal facility. The slightly deviated rays are penetrating, and excite secondary radiations when leaving the aluminium. The very deviable rays are stopped and

give rise to points affected by an intense secondary radiation.

One only of the two categories of non-deviable rays appears in the form of two fine lines opposite the source; these are very penetrating rays, the others were arrested quite near the source.

Another picture shows the simple beam obtained by a double series of openings; by one of them we can sometimes pass two distinct trajectories.

The third figure is of interest, as it shows the straight beam traversing, without deviation, a sheet of aluminium placed obliquely to the line of trajectory; and, finally, the fourth one shows the transmission of simple rays through aluminium, and the secondary effects they produce.

The same method has enabled me to observe that the secondary rays were themselves deviated by the magnetic field, in the same way as the exciting rays.

The radiations from radium also comprise some which are very penetrating, consisting of the least deviable and the non-deviable rays, of which the properties seem to be the same as Röntgen rays. These penetrating rays are but very slightly absorbed, and consequently their action on a photographic plate or on the air is very feeble, so that, by the preceding methods, we can get no very exact idea of their intensity. If we interpose in their path a very absorbent screen, they traverse it partially, but at the same time they become partially transformed into more absorbable rays. This transformation recalls that of fluorescence, and, through the secondary action, the effect immediately behind the screen is stronger than if this latter was not there. The photographic plate receiving the radiations—filtered through a thickness of lead of 1 c.m.—gives a stronger impression through a sheet of lead of 1 m.m. thickness than in the uncovered regions. The diagram shows the effect of the radiations coming from the sides of a leaden box after having traversed 5 to 12 m.m. of the metal.

These secondary phenomena may partially account for the appearance of shadows given by the edges of all the transparent screens placed over the photographic plates.

All the facts I have just related have exclusively to do with the obscure radiations which traverse opaque bodies, such as metal, glass, mica, &c. But there exists also another, quite different, phenomenon, of which the effects are arrested by glass and mica; they are comparable to those produced by a vapour of a special nature. This phenomenon was discovered in 1899 by Mr. Rutherford and by M. and Mme. Curie simultaneously.

Mr. Rutherford, while examining the radiations from thorium, observed that, besides the ordinary rays, there was another effect produced by an "emanation" consisting of a sort of vapour ionising the air. This vapour is deposited on bodies, principally those electrified negatively, and makes them momentarily radio-active. Mr. Rutherford made some very interesting measurements of this phenomenon.

At the same time, M. and Mme. Curie discovered that, under the influence of radium, bodies became temporarily radio-active. This is not the secondary effect already described, but a persistent phenomenon which disappears comparatively slowly from the moment when the action of the radium ceases. M. Curie has called this "induced radio-activity," and has made a very complete examination of it. He has observed that the phenomenon is produced with great intensity in a closed space, that induced activity is the same on all bodies and practically independent of the pressure inside the enclosed space, but that the phenomenon is not produced if we maintain a complete vacuum by removing the gases produced; solutions of salts of radium produce the same effect with greater intensity than the solid salts. Liquids, water of crystallisation extracted from active salts, or the water separated from an active solution by a semi-permeable membrane of celluloid, remain strongly radio-active; it is the same with the gases. These excited bodies produce the same effects as radium; they emit a penetrating ray

which traverses the glass vessels which contain them and makes these latter luminous. Induced activity is gradually propagated in gases in a sealed tube, even through capillary tubes and imperceptible cracks; bodies are excited the more as the volume of gas is greater in proportion to their surface. Phosphorescent bodies become luminous when excited. In a recent work, MM. Elster and Geitel have observed that atmospheric air has properties analogous to those of excited gases, and they have been able to collect on wires negatively electrified, traces of radio-active products. The cause of this radio-activity is a problem of the greatest interest.

Finally, there is a remarkable method of induction, which is of such a nature as to demand the greatest reserve in the conclusions which might be formulated relative to the presence of new elements in radio-active bodies. Every inactive substance which has been added to a solution of a uranium or radium salt, and which has subsequently been removed by precipitation, has become radio-active, and loses this radio-activity very slowly. This fact was first observed by M. Curie and M. Giesel, who rendered bismuth radio-active in this manner. In the case of uranium, a trace of barium, precipitated in the form of sulphate, became notably more active than the uranium; barium thus excited emits only deviable rays, like uranium.

After this precipitation the uranium salt, brought back to the solid state, is less radio-active than before; this loss of radio-activity can even be accentuated by successive operations, but the products gradually and spontaneously regain their original activity. The temporary diminution of activity after solution is a general fact for salts of uranium and radium. With salts of actinium M. Debierne has communicated a very great activity to barium. The barium thus excited can be separated from inactive barium; it can be fractionated like radiferous chloride of barium, the most active portions being the least soluble in water and hydrochloric acid. M. Debierne in this manner obtained a product a thousand times more active than uranium. Barium thus excited behaves as a false radium, but it differs from true radium in the absence of the spectrum and in gradually losing its power with time.

Among the radio-active preparations a large number may be temporarily excited bodies. Such is the case with "polonium," which is apparently only excited bismuth.

Uranium and radium are characterised by their emission spectra and by the stability of their radio-activity. The spontaneous activity observed in the case of different salts after solution, might find an explanation in a phenomenon of auto-induction of the active molecules on the inactive one they are associated with.

The origin of the radiant energy of these radio-active bodies is still an enigma. By the material hypothesis it does not appear unreasonable, by applying the phenomenon of the evaporation of an odoriferous body, to compare the emanation to a sort of gas, of which the molecules would have masses of the same order of size as electrolytic ions, and to identify the radiations with the cathodic rays resulting from the dislocation of these ions, and causing at the same time the emission of X rays. We might thus ascribe the expenditure of energy to the dissipation of active matter. Although this hypothesis will account for most of the known facts, still there does not exist any precise experiment which sanctions it.

I must not, however, dwell longer on this subject, of which I have incompletely summarised the present position, by emphasising the physical part, which comes more especially within my province, although the chemical side has given rise to work of the greatest interest.

These questions have raised new hopes on the transformation of matter. Besides the exceptional conditions under which they enable us to examine the cathodic rays, they have raised, and continue to raise, fresh problems every day of which the first and most mysterious is the spontaneity of the radiations.

ACTION OF HYDROGEN ON SULPHIDE OF MERCURY.

By H. PÉLABON.

CRYSTALLISED sulphide of mercury, from which all the free sulphur it might contain has been removed, is attacked by hydrogen at a relatively low temperature. The reaction is quite distinct at 280° , but it is very slow.

Having placed some sulphide of mercury and hydrogen in a sealed tube, we found that, after heating to 280° for forty-five days, the gas, brought rapidly to the normal temperature of the laboratory, contained 17 per cent of sulphuretted hydrogen. We cannot be at all certain that this proportion would not have increased if we had continued the experiment.

For the purpose of examining the reduction of sulphide of mercury by hydrogen at temperatures above 280° , we used the method of rapid cooling which we described in our research on selenide of mercury (*Bull. Soc. Chim.*, Series 3, xxiii., p. 211).

Two distinct cases may be observed in the reduction of sulphide of mercury; it can be effected in closed tubes either in the presence of an excess of liquid mercury or in the absence of that metal.

1. The Sulphide of Mercury is accompanied by an Excess of Mercury.

At 360° we obtained the following results, ρ being the relation between the partial pressure of the sulphuretted hydrogen and the total pressure; this proportion being expressed in hundredths.

Time of heating.	Value of ρ .
Hours.	
5	10.69
24	26.61
48	50.12
74	73.51
94	78.78
144	79.30
342	78.11
480	78.50

The quantity of sulphuretted hydrogen formed at 360° thus tends towards a limit, characterised by the value 78.67 for ρ . This limit is reached after about ninety hours heating; its existence is due to the fact that the sulphuretted hydrogen and the mercury are able to react on each other under the same conditions of temperature. We placed some pure mercury and sulphuretted hydrogen in sealed tubes, and kept them at 360° . The results were:—

Time of heating.	Value of ρ .
Hours.	
6	91.39
15	79.92
192	79.29
215	78.91

Thus we again find a limit very near to that given by the direct action of the sulphide on hydrogen. It is as well to mention that the value of ρ does not depend either on the mass of the sulphide or the mass of the mercury, so long as these bodies are not entirely reduced to vapour at the temperature of the experiment. Neither has the pressure of the hydrogen gas any influence, as is distinctly shown by the following figures:—

Pressure of H at 0° .	Time of heating.	Value of ρ .
M.m.	Hours.	
759	144	78.45
761	144	78.10
384	144	78.60
390	210	78.90
195	215	79.12

When the temperature increases, the limit value of ρ also increases. Thus, at 440° , we found:—

Time of heating. Hours.	Value of ρ .
2	44'48
14	85'25
24	85'18
43	85'41
144	85'20

Thus ρ reaches a limit of about 85'26 in a much shorter time than at 360°, as equilibrium may be considered as reached at the end of fourteen hours.

At 540° a value of about 92'10 was obtained for ρ . Finally, when the temperature is raised to above 540°, ρ has values which slightly pass the preceding figures. Thus, after four hours' heating, we found:—

At 585°	$\rho = 92'13$
„ 590°	$\rho = 92'00$
„ 610°	$\rho = 92'81$

It is probable that, under these conditions of temperature, the method of rapid cooling does not give the exact composition of the gaseous mixture, the speed of the reaction becomes of the same importance as the speed of cooling. To sum up, we have—

At 360°	$\rho = 78'67$
„ 440°	$\rho = 85'29$
„ 540°	$\rho = 92'10$

Thus the quantity of sulphuretted hydrogen goes on increasing with the temperature. This result is in complete accord with the law of the displacement of equilibrium by variations of temperature if we admit the following equation:—

$\text{HgS (solid)} + \text{H}_2 \text{ (gas)} = \text{H}_2\text{S (gas)} + \text{Hg (liquid)}$, which at 15° is accompanied by an absorption of heat, and is still endothermic at the temperature of our experiments.

2. The Sulphide of Mercury is not accompanied by an Excess of Mercury.

When we react with hydrogen and sulphide of mercury alone, two cases may occur; either the vapour-tension of the liberated mercury attains the maximum value or it remains lower than the tension of the saturating vapour.

In the first case, we have a recurrence of the system already examined; in the other, we have to study the equilibrium which is established between the following bodies:—Mercury vapour (the non-saturating vapour), solid sulphur, sulphur vapour (the saturating vapour), hydrogen, sulphydric acid.

In a general way, at a determined temperature and at an initial pressure of the hydrogen gas (also previously decided upon), the limit of proportion ρ is higher than the value ρ_1 of the same proportion which would be obtained when operating in the presence of an excess of mercury. The temperature remaining invariable, ρ diminishes as the pressure increases, but its value never gets lower than ρ_1 .

At 300° we obtained the following figures:—

(a) The pressure of the hydrogen gas introduced into the tubes was about the normal pressure when measured at 0°.

Time of heating. Hours.	Pressure. M.m.	Value of ρ .
144	759	78'95
107	768	78'27
212	757	78'32

(b) The pressure of the hydrogen gas was about 380°.

157	387	78'75
225	390	78'11
212	389	78'63

(c) The pressure was about 190 m.m.

215	195	79'10
224	189	78'70
251	187	79'32

According to these results, the value of ρ would vary

very little with the pressure; only the figures of the last series (c) were a little higher than the value $\rho_1 = 78'67$ which we found in the first set of experiments.

Remarks.—It is easy to show that, starting with sulphide of mercury and hydrogen at a pressure of 760 m.m., we arrive at a system which should contain liquid mercury, provided the temperature is up to 360°. According to the equation of the reaction, the vapour-tension of the mercury set at liberty should be equal to the partial pressure of the hydrosulphuric gas, since the two bodies are formed simultaneously in equivalent proportions, as the H_2S represents two volumes of Hg.

The vapour-tension of the mercury should be therefore—

$$f = H \times \frac{\rho}{100} (1 + \alpha t) \quad \dots \quad (1),$$

α being the coefficient of dilatation of the gases at constant volume, t the centigrade temperature of the experiment, and H the pressure at 0° of the hydrogen gas originally introduced into the tube.

According to experiment, ρ has a value of about 78'6 when $t = 360^\circ$. Thus, if $H = 760$ m.m., we have—

$$f = 760 \times 0'786 \times (1 + 0'00367 \times 360),$$

or—

$$f = 760 \times 1'82.$$

But the tension of the saturating mercury vapour at 360° is about 760 m.m. = F ; thus we get $f > F$, which cannot take place. A part of the mercury rapidly condenses to the liquid state, and we come back to the system examined before, and consequently we obtain the same limit for ρ .

The equation (1) enables us to calculate the pressure limit above which the mercury will be deposited, and below which it will remain in the state of a non-saturating vapour; it suffices to replace f by F , and ρ by the figure found in the first experiments; in this manner we get, if $F = 760$ m.m.,—

$$760 = H \times 0'7867 (1 + 0'00367 \times 360),$$

from which we have—

$$H = 416 \text{ m.m.}$$

For pressures lower than 416 m.m., we ought to find different values for ρ from those obtained for pressures above this limit; this is exactly what happens if we refer to the results of the experiments made at pressures of about 190 m.m. At 440° we obtained the following results:—

(a) The pressure of the hydrogen gas is about normal.

Time of heating. Hours.	Pressure. M.m.	Value of ρ .
2	752	44'58
5	761	81'94
10	767	88'56
15	763	90'27
24	757	90'02
45	763	90'63
112	758	90'72

The equilibrium, reached after about fourteen hours, is characterised by a value for ρ of about 90'65.

(b) The pressure of the hydrogen was about 380 m.m.

2	375	68'36
8	382	94'06
12	387	94'51
18	377	94'23
48	384	94'36

The limit value of ρ is about 94'36.

(c) The pressure is about 190 m.m.

24	193	96'12
162	187	96'81
45	195	96'75
210	185	97'01

The average limit value of ρ is not more than 96'67. We made certain in every case that equilibrium was reached.

At 540° the pressure of the hydrogen was about the same as that of the atmosphere, and we obtained the following results:—

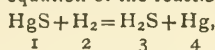
Time of heating. Hours.	Pressure. M.m.	Value of ρ .
$\frac{1}{2}$	761	97.19
14	756	97.84
72	763	97.00

The limit corresponds to $\rho = 97.34$ (about).

For pressures below 760 m.m. the limit of ρ is above 97; it cannot, however, be measured with great accuracy, as the amount of the gaseous mixture to be analysed is very small—2 to 4 c.c. Finally, if the temperature exceeds 540°, ρ keeps a very nearly constant value of about 97.5.

Theoretical Considerations.—The figures found in the above experiments enable us to submit a relationship established by thermodynamics to the control of experiment—a relationship which has already been verified up to a certain limit by the figures obtained in the examination of the action of hydrogen on selenide of mercury.

If we write the equation of the reaction—



applying the figures 1, 2, 3, 4 to the four bodies which take part in it, we can easily see that the general relation (1) which exists between the partial pressures of the gases and vapours contained in the system takes the form—

$$\log. \frac{\rho_1^2 v}{\rho_3^2} \frac{\rho_2^2 v}{\rho_4^2} = F(T) \quad (2).$$

$2v$ is the volume occupied by the whole of the molecules of the simple and compound bodies. If the pressures are nil, we simply write—

$$\frac{\rho_1 \rho_2}{\rho_3 \rho_4} = f(T) \quad (3).$$

Let us now see how this proportion will apply to each particular case examined.

1. In the reaction of hydrogen on sulphide of mercury in the presence of an excess of mercury, the pressure, ρ_4 , of the mercury vapour is equal to the tension of the saturating vapour of this liquid. Let F be the tension, which is a function of the temperature only, the pressure, ρ_1 , is also uniquely a function of the temperature for the same reason, since we operate with an excess of sulphur; we can therefore say—

$$\frac{\rho_2}{\rho_3} = x(T) \quad (4)$$

or—

$$\rho_1 = \frac{100 \rho_3}{\rho_2 + \rho_3} = \frac{100}{1 + x(T)}.$$

ρ_1 depends only on the temperature, and not on the pressure; this result is quite in accord with those obtained by experiment. We have seen, in fact, that no matter what the pressure was, we obtained, under the conditions indicated, $\rho_1 = 78.67$ at 360°, $\rho_1 = 85.26$ at 440°, &c.

2. If the hydrogen is made to react on sulphide of mercury alone we get—

$$\rho_1 = \phi(T) = P_1;$$

and, further, the equation of the reaction shows that at each instant we have—

$$\rho_3 = \rho_4 = P_3.$$

The proportion (3) then becomes—

$$\frac{P_2}{P_3^2} = \psi(T) \quad (5).$$

The examination of this formula shows that the proportion of sulphuretted hydrogen gas in the mixture increases when the total pressure diminishes. The partial pressure

of the hydrosulphuric gas and the total pressure, π , should, further, verify the following equations, which are deduced from the formula (5), $\pi = P_2 + P_3$:—

$$\frac{\pi - P_3}{P_3^2} = \frac{\pi' - P_3}{P_3^2} = \frac{\pi'' - P_3}{P_3^2} = \dots = \psi(T) \quad (6).$$

We were able to determine, as has been shown, the corresponding values of ρ_2 for several different values of π . We repeat the values of this relationship, and place opposite those that the equations (6) enable us to calculate:—

Pressure of gas, π . M.m.	ρ_2 observed.	ρ_2 calculated.
758	90.65	—
386	94.36	94.73
187	96.67	96.84

The calculated figures are, as can be seen, slightly higher than those found by experiment; in spite of that, however, the concordance is fairly satisfactory.

Remarks.—When the system contains mercury in excess we can, in fact, write—

$$\frac{\phi(T) \rho_2}{\rho_3 F} = f(T) \quad (7).$$

When, on the contrary, we make the hydrogen act on the sulphide alone, we have—

$$\frac{\phi(T) P_2}{\rho_3^2} = f(T),$$

from which we deduce—

$$\frac{P_2}{P_3^2} = \frac{\rho_2}{\rho_3^2 F}.$$

F is given in tables of vapour tensions; it is equal to 2934 m.m. at 440°, $\frac{P_2}{P_3^2}$ can be calculated from the results of the experiments. We then find—

$$\rho_1 = 100 \frac{\rho_3}{\rho_2 + \rho_3} = 85.61,$$

a figure which is very close to that found by experiment, which was $\rho_1 = 85.26$.

The experimental verification of the relation (3) can be pushed further by examining the action of sulphuretted hydrogen on mercury.

Action of Sulphuretted Hydrogen on Mercury.

Sulphuretted hydrogen gas attacks mercury, giving a sulphide which can exist in the form of a non-saturating vapour; it is easy to see theoretically that, other things being equal, the limit value of ρ should be lower under these conditions than that obtained when the system contained an excess of sulphide of mercury. In fact, we get, according to the equation of the reaction,—

$$\rho_1 = \rho_2 = \omega_2, \quad \rho_4 = F.$$

The proportion (3) is therefore written—

$$\frac{\omega_2^2}{\omega_3 F} = f(T) \quad (8).$$

ω_2 cannot be equal to the tension of the saturating vapour of the sulphide of mercury, without which we should again obtain the results of the first examination; now, this is not the case. Therefore, we necessarily have—

$$\omega_2 < \phi(T),$$

from which, allowing that we get—

$$\frac{\omega_2^2}{\omega_3 F} = \frac{\phi(T) \rho_2}{\rho_3 F},$$

we find the inequalities—

$$\frac{\omega_2}{\omega_3} > \frac{\rho_2}{\rho_3} \text{ and } \frac{\omega_3}{\omega_2 + \omega_3} < \frac{\rho_3}{\rho_2 + \rho_3}.$$

The pressure of the sulphuretted hydrogen gas being about 760 m.m. at 0°, we find at 440°—

$$\rho_3 = 100 \frac{\omega_3}{\omega_2 + \omega_3} = 80.46.$$

The value of ρ_3 is therefore decidedly lower than the value $\rho_1 = 85.26$.

The results of experiments at 440° are as follows, the pressure being about 760 m.m. :—

Time of heating. Hours.	Value of ρ .
2	95.00
15	82.80
24	81.86
72	80.14
96	80.57
112	80.67

At 540° we have already found that ρ_1 has a value slightly different to 92.10; by examining the action of sulphuretted hydrogen on mercury we found, with a pressure of about 760 m.m.,—

Time of heating.	Value of ρ .
5 minutes	97.11
10 "	88.48
15 "	84.65
25 "	84.27
12 hours	84.30

We thus again get distinctly $\rho_3 < \rho_1$. A quantitative verification could be made if we knew the tension of the saturating vapour of sulphide of mercury at each temperature.—*Bull. Soc. Chim.*, Series 3, xxv., No. 16.

ON THE SULPHURIC AND DISULPHURIC ANHYDRIDES.

By G. ODDO.

THE present ideas entertained regarding sulphuric anhydride are meagre and contradictory. According to Marignac (*Arch. Soc. Phys. Nat.*, 1833, vol. xxii., p. 255; 1875, vol. lii., p. 236) the two known modifications of this substance—the prismatic which melts at 18° and boils at 46°, and the fibrous, which is infusible, and changes into the prismatic form at 100°—are isomeric. According to Schultz-Sellak (*Bull. Soc. Chim.*, vol. xiv., p. 154; *Berichte*, vol. iii., p. 215), the second is the polymer of the former.

Buff (*Liebig's Ann.*, 4th Supplement, p. 127), and, later on, Weber (*Pogg. Ann.*, vol. clix., p. 313; *Berichte*, vol. xix., p. 3187), having shown that the prismatic product changes into the fibrous product only when it absorbs water, even a trace only, affirm that only a single modification of sulphuric anhydride exists, viz., the prismatic, fusible at 15°, of which the other is only a product of hydration. This opinion, attacked by Marignac (*Arch. Soc. Phys. Nat.*, [2], vol. lviii., p. 228), has been adopted by Rebs (*Bull. Soc. Chim.*, 1889, vol. i., p. 717; *Lieb. Ann. Ch.*, vol. ccxvi., p. 356—382).

Finally, Ostwald, in his recent treatise on inorganic chemistry (*Grundlinien Anorg. Chemie*, p. 292) considers the two modifications as a case of polymorphism analogous to the two monochlorides of iodine. But still more regrettable than this diversity of opinion is the ignorance we must admit as to the identity or the difference of their chemical properties.

Wishing to attack this question, I have determined the molecular weights of the two modifications in solution in oxychloride of phosphorus; I found that the prismatic variety melts at 13.8°, and answers to the simple formula SO_3 , the fibrous variety having the double formula S_2O_6 . Further, I have noticed considerable differences in their chemical properties.

In the following lines I shall call the first modification sulphuric anhydride, and the second disulphuric anhydride.

Sulphuric Anhydride.

I prepared this anhydride by heating Kahlbaum's crystallised, fuming, sulphuric acid very slowly on the sand-bath, in a retort fitted with a ground glass stopper, to which was attached a small receptacle terminating with a point about 1 decimetre in length, plunged into the sulphuric acid. During the distillation this receptacle was kept in a water-bath at 30°, and when a desired quantity of the anhydride was collected, the two ends of the receptacle were fused before the blowpipe after removing it from the retort. I thus prepared two collectors each time, and these were kept constantly at 30° during the determinations, a temperature at which sulphuric anhydride is not polymerised.

As I have shown in a previous paper (*Reddiconi R. Accademia Lincei*, 1901, p. 453) oxychloride of phosphorus always contains products of hydration, which cannot be completely eliminated, either by distillation or crystallisation; further, there are always traces of moisture in the apparatus. To prevent all cause of error it is necessary to dehydrate everything. I succeeded in doing this very easily by using sulphuric anhydride itself in the following manner:—To a known quantity of the solvent contained in a cryoscope furnished with a stirrer, and carefully protected from the moisture of the atmosphere, I added one or more drops of the sulphuric anhydride from one of the collectors already prepared, but not weighed; it sometimes happens, if the oxychloride used contains too much moisture, that the first few drops cause an elevation of the point of congelation of the solvent; in this case we add a few more drops of sulphuric anhydride to obtain a considerable lowering of the congelation-point; I adopted this temperature as the congelation-point of the solvent, and I determined that from this point successive additions of anhydride caused lowerings of this point proportional to the concentration.

To make the determination, I use the anhydride from the second tube, which I weighed in a weighing bottle; by means of a file, I cut off the end of the tube; this I kept in the bottle, and poured the desired quantity of anhydride into the cryoscope. I then again sealed up the end of the tube, and made the cryoscopic determination. If in these various operations one is helped by a skillful assistant, almost every source of error can be guarded against. The following are the results obtained:—

First Determination.—The oxychloride crystallised at 3.928° by a Beckmann differential thermometer. After adding the unweighed sulphuric anhydride it crystallised at 3.458°; this figure was taken as the crystallising-point of the solvent. On adding the weighed quantity of sulphuric anhydride the point of congelation was found to be 1.362°.

By adopting the figure 69 (G. Oddo, *loc. cit.*) as the constant of the oxychloride of phosphorus we have:—

Concentration	2.2902
Lowering of the congelation-point ..	2.096°
Molecular weight	75.4

Second Determination.—The solvent crystallised at 3.812°, and after the addition of the unweighed sulphuric anhydride, at 2.310°. On then adding the weighed quantity of anhydride, we obtained for the point of congelation 0.488°. Therefore:—

Concentration	2.0643
Lowering of the congelation-point ..	1.822°
Molecular weight	78.1

For SO_3 the calculated molecular weight = 80.06.

Disulphuric Anhydride.

This was prepared by carefully distilling disulphuric acid on the sand-bath, and collecting the product at 10—13°;

it polymerises rapidly, but the polymerisation is not complete until after the lapse of several days.

The fibrous mass was cut, at the bottom of a deep mortar, with a pair of well-polished steel scissors, which are not attacked, and I kept the various pieces in weighing bottles; if they were all kept in the same bottle they would join together again and form one mass.

By means of platinum or even bone forceps, which are not attacked, the fragments can be easily transferred from the weighing bottle to the cryoscope.

In making the determinations I again dehydrated the oxychloride, and, at the same time, the apparatus, by dissolving unweighed pieces of the anhydride in the liquid, in sufficient quantity to cause a decided lowering of the congelation-point. The solution of this anhydride must be effected rather slowly, and it is necessary to keep on stirring.

The following are the results obtained:—

First Experiment.—The solvent crystallised at $4^{\circ}21'2''$, and after the addition of the unweighed fibrous anhydride at $2^{\circ}32'9''$, a temperature which I adopted as the congelation-point. By then adding the weighed quantity of fibrous anhydride the crystallisation took place at $2^{\circ}14'5''$.

Concentration.. .. .	1.9322
Lowering of the congelation-point ..	0.784°
Molecular weight	170.05

Second Experiment.—The following determinations were made in series, still the values obtained are sufficiently concordant; this proves the accuracy of the method.

The solvent crystallised at $4^{\circ}89'8''$, and after the addition of the unweighed fibrous anhydride at $4^{\circ}56'9''$.

Concentration.	Lowering of the congelation-point.	Molecular weight.
2.0360	0.843°	166.6
3.1505	1.347°	161.38
3.8400	1.682°	157.5

The calculated molecular weight for S_2O_6 is 160.12.

Third Experiment.—Finally, I will give a series of experiments made with the fibrous anhydride prepared some hours before the cryoscopic examination, but still having the appearance of a compact fibrous mass. The solvent crystallised at $3^{\circ}62'5''$, and after the addition of the unweighed fibrous anhydride at $3^{\circ}15'5''$.

Concentration.	Lowering of the congelation-point.	Molecular weight.
1.0893	1.119°	122.66
4.0609	2.365°	118.47
4.4510	2.543°	120.77

Differential Characteristics between Sulphuric Anhydride and Disulphuric Anhydride.

These anhydrides, besides their already known physical properties, differ in several chemical points. I will here only mention the following facts.

First of all, as a dehydrating material sulphuric anhydride is much more active than disulphuric anhydride. If, for example, we let a drop of sulphuric anhydride fall on an organic tissue, the latter is immediately carbonised; in the case of animals, very deep ulcers are formed; on the other hand, disulphuric anhydride does not affect organic tissues, that is if the contact is not sufficiently prolonged as to allow of hydration from the atmosphere. I have squeezed this anhydride between my fingers without suffering the least inconvenience. A fact already observed by Schulz-Sellak, is that sulphuric anhydride dissolves immediately in sulphuric acid; on the other hand, disulphuric anhydride dissolves very slowly. I have observed further that if the sulphuric acid has been well-cooled, when pieces of disulphuric anhydride and a few pieces of ice are thrown into the acid together, no energetic action takes place; the anhydride dissolves slowly, and only after several minutes, but with continual stirring we eventually get complete solution.

The same thing occurs with organic substances, if we take care to avoid all sudden increases of temperature which, causing the rapid dissociation of the disulphuric anhydride into sulphuric anhydride, would cause the effects of the latter to be attributed to the former.

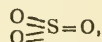
To cite one example only, sulphuric anhydride reacts energetically and very quickly on powdered camphor, which is partly carbonised, and partly transformed into a liquid body; on the other hand, by making an intimate mixture at the ordinary temperature of disulphuric anhydride and powdered camphor, nothing in particular is observed, and it is only after having triturated the mixture for some time that the reaction takes place; but as soon as it commences, the disengagement of heat is so great that it causes the instantaneous dissociation of all the disulphuric anhydride into sulphuric anhydride. The reaction then takes place rapidly, as in the case when sulphuric anhydride was used, and the final result is the same. I will also mention a few new facts concerning these two anhydrides, which will show how necessary and interesting the thorough examination of these substances is, a research which I propose to continue.

Sulphuric anhydride does not react on the metals; if a few drops of this anhydride, poured into a test-tube, are placed in contact with various metals, we observe that sodium and potassium float thereon, and the other metals, such as Mg, Zn, Cu, Sn, Pb, Ni, and Cd, all in the form of powder, and Hg, &c., sink without any reaction taking place.

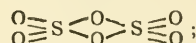
In the same manner the oxides of the metal do not react with sulphuric anhydride at the ordinary temperature; I have tried HgO , SnO , CuO , ZnO , PbO_2 , BaO , and Na_2O always with negative results.

Disulphuric anhydride, at the bottom of a test-tube exposed to the air, remains almost unchanged for several days; a part of it sublimes and reaches a certain height, where a white cloud is formed which, in spite of agitation, will not rise further, and protects the anhydride remaining underneath from the action of the moisture in the atmosphere. Sulphuric anhydride left at the bottom of a test-tube is soon transformed into disulphuric anhydride.

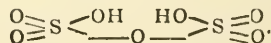
While postponing theoretical considerations to a future and more complete paper I will here remark that if we consider the atom of sulphur as a hexad, the formula for sulphuric anhydride will be:—



and that of disulphuric anhydride:—



the first term of hydration of this latter is disulphuric acid—



Further, if we admit that the atoms of oxygen have the form of an elongated ellipsoid and are disposed symmetrically round the atom of sulphur, as if on the sides of an equilateral triangle of which the sulphur occupies the centre, we can easily see why sulphuric anhydride is stable above 27° and polymerises below that point; the three atoms of oxygen, in their vibrations at a low temperature, move in the direction of their extremities; this results in a tension which, by analogy with the trimethylene compounds, may be called external; it is for this reason that any disturbing cause, such as traces of moisture, suffices to turn round the atom of oxygen, with the formation of a radicle which unites with another identical radicle giving a molecule of disulphuric anhydride. The opposite happens when a high temperature acts on this latter anhydride; and for this reason it is dissociated into two molecules of sulphuric anhydride.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 20.

A NEW INVESTIGATION CONCERNING THE ATOMIC WEIGHT OF URANIUM.*

By THEODORE WILLIAM RICHARDS
and
BENJAMIN SHORES MERIGOLD.†

Introduction.

OUR knowledge of uranium dates from the year 1789, when it was first recognised as an element by Klaproth. It can by no means, therefore, be classed with the new elements, nor is it of great rarity. Nevertheless, comparatively few determinations of the atomic weight of this element have been made, and of these, one only has been carried out with the degree of accuracy necessary in work of this kind. During the fifty years following the discovery of uranium a number of atomic weight determinations were made by Berzelius, Arfvedson, Schönberg, Marchand, and Rammelsberg. This early work is now of historical interest only, for the results vary widely, and in some cases are of such a nature as scarcely to be considered quantitative, in the modern sense of the word. For example, Rammelsberg obtained results varying from 184 to 234, calculated upon the modern basis.

In 1841 Péligot discovered that the substance then known as uranium was not an element, but an oxide. This discovery, while it did not impair the value of the analytical work previously done, necessitated a re-calculation of the numerical value of the atomic weight. The new value was 120, and this remained practically unchanged during the next thirty years. When the periodic classification of the elements was first suggested, uranium, with the atomic weight 120, was one of the elements for which there was no place. From a study of the properties of uranium and its compounds, Mendeléeff declared that the atomic weight of uranium was probably 240 instead of 120 (*Annalen der Chemie u. Pharmacie*, Supp. Vol. viii., 178 *et seq.*). The question was not definitely settled until Zimmermann, in 1885, carried out the suggestions of Mendeléeff, and by specific heat and vapour density determinations confirmed the higher value (*Annalen der Chemie u. Pharmacie*, ccxvi., 1).

Owing to the wide variations in the published results, the atomic weight of uranium has long been considered one of the least satisfactorily determined of the atomic weight values. A glance at the results thus far obtained is sufficient to show the need for further work in this line. A complete *résumé* of the older work upon the subject is to be found in Clarke's recent work on the atomic weights ("A Re-calculation of the Atomic Weights," by F. W. Clarke, *Smithson. Misc. Coll.*, "Constants of Nature," 1897, Part V., 263). The following table summarises those investigations which seem to possess even a little quantitative value:—

Less Inaccurate Previous Work on the Atomic Weight of Uranium.

O = 16.000.

1841. Péligot (<i>Compt. Rend.</i> , xii., 735; <i>Ann. Chim. Phys.</i> , 1842, [3], v., 5).—Analysis of green chloride	240.0±
1842. Ebelmen (<i>J. Prkt. Chem.</i> , 1842, xxvii., 385).—Combustion of oxalate	238.0±
1843. Wertheim (<i>J. Prkt. Chem.</i> , 1843, xxix., 209).—Double acetate of sodium and uranium	239.0±
1846. Péligot (<i>Compt. Rend.</i> , 1846, xxii., 487).—Combustion of oxalate and acetate	240.0±
1886. Zimmermann (<i>Ann. d. Chem.</i> , 1886, ccxxxii., 299).—Reduction of oxide, U ₃ O ₈ to UO ₂	239.6
1886. Zimmermann (<i>Ann. d. Chem.</i> , 1886, ccxxxii., 299).—Ignition of double acetate	239.5

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxvii., No. 14.

† The greater part of the work described in this paper was presented to the Faculty of Arts and Sciences of Harvard University by B. S. Merigold, as a thesis for the degree of Ph.D., in June, 1901.

The work of Ebelmen, Wertheim, and the early work of Péligot is necessarily of little weight in assigning a probable value to the atomic weight of uranium. In some cases the material used was impure, and in others the methods of analysis were faulty. Consequently, it is not surprising to find differences of whole units in the individual determinations of each series.

Péligot's later determinations from the oxalate is perhaps the best of the early work. His material was carefully purified, and his method is far preferable to the work of Ebelmen and Wertheim. By combustion analysis he determined the ratio between uranium oxide and carbon dioxide. Thus he eliminated the error involved in weighing a crystallised salt which would probably contain more or less included water. The principal sources of error are the questionable use of combustion analysis in atomic weight investigations, and the possibility of unoxidised carbon remaining in the uranium oxide. His best results vary from 239.4 to 241.1.

The work of these chemists, though a great improvement over the attempts of Rammelsberg and the other early workers, leaves much to be desired, and does little more than give an approximate idea of the probable value of the atomic weight of uranium.

Zimmermann's investigation of the ratio between the oxides UO₂ and U₃O₈ was much more carefully carried out, and is the only work thus far published that is worthy of serious consideration. Using carefully purified material, and giving attention to detail, Zimmermann oxidised the lower oxide by means of a stream of oxygen, and observed the gain in weight. His results for the atomic weight varied from 239.49 to 239.76, an extreme difference of 0.27, or 0.11 per cent. The average was about 239.6. The chief probable cause of error in this method is the difficulty which is always experienced in forming a more voluminous solid from a less voluminous one. Uranous oxide has a specific gravity of 10.2 while the "uranoso-uranic" oxide has a specific gravity of only 7.3. The great increase of volume which occurs when the higher oxide is formed must tend to protect particles of the lower oxide from the action of the oxygen. Hence the gain in weight will be too small, and the apparent atomic weight of the metal too large (compare Richards and Baxter, *Proc. Amer. Acad. Arts Sci.*, 1898, xxxiv., 351; *Ztsch. Anorg. Chem.*, 1899, xxi., 251). It is clear that a very small deficiency in the weight of the higher oxide must cause a great increase in the apparent atomic weight.

Moreover, any incompleteness in the reduction by which the lower oxide was prepared, or any retention or occlusion of gases within this oxide, would also tend to raise the apparent atomic weight. Hence one is inclined to believe, even without further evidence, that Zimmermann's result for uranium must be too high.

A new determination of the atomic weight of uranium has recently been made by J. Aloy (*Comptes Rendus*, 1901, ccxxii., 551).* The method employed differs materially from any previously used in uranium work. The values obtained are derived from the ratio between the weight of nitrogen and that of uranous oxide contained in crystallised uranyl nitrate. Uranyl nitrate was purified by repeated crystallisation. A quantity of the pure nitrate, the weight of which need not be known, was put into a boat, and the boat surrounded by a section of platinum tube, to prevent loss of material. The whole was placed in a combustion tube between spirals of reduced copper. One end of the combustion tube was connected with a carbon dioxide generator, and the other with an absorption apparatus containing a concentrated solution of potash.

After sweeping the air out of the apparatus with a current of carbon dioxide, the nitrate was heated so long as evolution of nitrogen occurred, the temperature being finally raised to red heat. The reduced copper was kept at red heat throughout the operation. When it was certain that no more nitrogen was evolved, the green oxide remaining in the boat was reduced by hydrogen to uranous

* This work is discussed rather fully here, since it is too recent to have been included in Clarke's book.

oxide and weighed. The nitrogen was transferred to a measuring tube reading to tenths of a cubic centimetre. From the ratio of the weight of this volume of nitrogen to the weight of the oxide, the atomic weight is calculated.

The following are the results of the eight determinations given:—

Atomic Weight of Uranium.

$N = 14.04$.

Volume of nitrogen, C.c.	Atomic wt. of uranium.
15.25	239.3
33.5	239.4
38.0	239.6
52.5	239.5
81.25	239.4
125.0	239.5
151.2	239.4
165.0	239.4

Average . . . 239.4

This method has the merit of simplicity, and does not involve the weight of the crystallised salt. There are, however, several sources of possible constant error that have not been taken into account. When crystallised uranium nitrate is heated, it first melts in its water of crystallisation. As in all similar cases, it requires the very greatest care to prevent spattering while the crystal water is being driven off. It was undoubtedly as a precaution against loss of material in this way that Aloy used his platinum tube. By the time the crystal water is expelled, the fused mass has hardened into a solid cake, changing in colour from yellow to orange, and finally to the green of urano-uranic oxide, U_3O_8 .

This method of preparing the green oxide from pure uranyl nitrate was used in the work to be described in the following pages. It was *invariably* found, however, that during the decomposition of the dried nitrate, and the subsequent oxidation, the oxide first produced forms a protecting crust, as it were. This prevents, or at least very materially retards, the decomposition of the material within the interior, *even when the temperature is maintained for several hours at red heat*. On the outside, the material had the appearance of being completely converted to oxide. On powdering the lumps, however, and again heating, there was *in every case* a further evolution of nitric fumes. Moreover, nitrogen itself is often retained by oxides prepared in this way (Richards and Rogers, *Proc. Amer. Acad. Arts Sci.*, 1893, xxviii., 200; also Richards, *Proc. Amer. Acad. Arts Sci.*, 1898, xxxiii., 399). It seems thus extremely probable that the quantities of nitrogen measured by Aloy were in every case too small. Obviously, until this point is definitely settled, Aloy's results must be regarded with more or less suspicion.

It has been pointed out that reduction is usually much more complete than oxidation (Richards and Baxter, *loc. cit.*). During the reduction of an oxide, there is formed, perhaps, by the removal of a portion of the oxygen, a kind of skeleton framework, giving to the remaining substance a porous structure which enables the reducing gas to penetrate farther into the interior of the mass, until reduction is complete. Owing to this action, it is probable that when the green oxide of uranium is finally reduced by hydrogen, all the nitrogen is expelled, and the final product is pure uranous oxide. Consequently, the weight of uranous oxide used in the calculation is probably nearly correct, the principal error being in the volume of nitrogen.

Aside from this special objection to the use of this method in its application to uranium, there is the general objection to the use of such a method where great accuracy is desired. The exact measurement of small quantities of gas offers considerable opportunity for error, especially when, as in this case, the gas is first to be transferred from the collecting to the measuring apparatus. When the volume or weight of a gas is

involved in an atomic weight investigation, it is customary to work with as large volumes as possible, thus reducing to a minimum the effect of the errors inevitably connected with the measurement of the gas. The exact measurement of a volume no larger than 165 c.c., even—the largest volume measured by Aloy—is a matter of considerable experimental difficulty, while with the smaller volumes, 15, 33, and 38 c.c., errors of at least 0.1 per cent are not only possible, but extremely probable. A difference of one-tenth of 1 per cent in the volume of nitrogen makes a difference of 0.3 in the value of the atomic weight. The errors of collection and transference of the gas are more likely to result in reading too small rather than too large volumes, giving too high values for the atomic weight.

From these considerations, it is evident that Aloy's results are at least somewhat doubtful. Aloy gives notice of his intention to apply this method to the determination of other atomic weights, but it is to be hoped that before doing so he will clear up some of the doubtful points in connection with the process. As carried out in this investigation, the method certainly is not a valuable addition to the methods of atomic weight determination.

From the earlier results Clarke computed the value 239.6, while the German Committee recommend 239.5. Both figures are practically identical with Zimmermann's figures.

The investigation herein described was undertaken with the hope that by increasing the experimental basis of our knowledge of the subject, we might be able to reduce to somewhat narrower limits our present uncertainty in regard to the real value of this constant.

(To be continued.)

NOTICES OF BOOKS.

Assaying and Metallurgical Analysis, for the Use of Students, Chemists, and Assayers. By E. L. RHEAD, Lecturer on Metallurgy, Municipal School of Technology, Manchester, and A. HUMBERT SEXTON, F.I.C., F.C.S., Professor of Metallurgy, Glasgow and West of Scotland Technical College. London, New York, and Bombay: Longmans, Green, and Co. 1902. Pp. 431.

THE present volume was written with the intention of providing the student, chemist, or assayer with a handbook sufficiently comprehensive to include the greater part of the work likely to be required in the laboratory or assay office. That the authors have achieved their object will be evident to anyone who looks through the book.

A work such as this is not intended so much for the mere student who is actually learning the subjects treated, but it is of great service to the assayer in general as a book of reference and laboratory companion.

The book is divided into three parts. Part I. deals with laboratory appliances and general processes, such as sampling, weighing, the management of furnaces, the reagents used in both dry and wet assaying, &c.

In Part II., which is the most important part of the volume, the general plan followed has been to consider under the name of each metal, (a), the materials and products in which its estimation is commonly required, accompanied by a short description of the same to make their identification easy; (b), the dry tests for, and the important chemical reactions of the metal, with, in some cases, special instructions for the detection of small quantities; (c), the methods of conducting the dry assay by fusion or otherwise, followed by applications to special materials where modifications are necessary; (d), methods of preparing solutions for the estimation of the metal; and (e), methods for gravimetric, volumetric, and colorimetric estimations.

Part III. is on metallurgical analysis, and commences with the analysis of alloys of all kinds, and the commoner metals, such as copper, zinc, tin, &c., in their commercial forms; this is followed by the analysis of iron ores, iron and steel, ferro-aluminium, chromium, tungsten, &c., slags and refractory materials; and, finally, the examination of coal, coke, and gaseous fuels.

There are five appendices, containing useful tables and special tests, such as the cyaniding tests for gold, tables for qualitative analysis, &c.

The book is well printed and bound, and the illustrations, though not numerous after the first part is concluded, are good, while the table of contents and the index are efficient and well carried out.

CORRESPONDENCE.

ANALYSIS OF TIN ORES.

To the Editor of the Chemical News.

SIR,—I read with interest the translation of J. A. Muller's paper on the above subject (*Bull. Soc. Chim.*, Series 3, xxv., No. 23) which appeared in the *CHEMICAL NEWS* of March 27th (vol. lxxxv., p. 147), and was pleased to find that the author's results fully confirm the reliability of the hydrogen-reduction method of assaying ordinary tin ores.

I have used the process for over thirty years, and do not hesitate to recommend it for general adoption in laboratories, as being far and away the quickest, the simplest, and the most accurate.

It is only fair to here mention that the first chemist to suggest the use of hydrogen in the analysis of tin ores was Dr. William McCowan, F.I.C., &c., who, in 1871, when we were brother students under Professor Arnulf Schertel, perfected the process which is now credited to other analysts.—I am, &c.,

R. W. EMERSON MACIVOR.

The Laboratory,
29, Fenchurch Street, E.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 11, March 17, 1902.

Heat developed during Reactions between Bodies in the Solid and Gaseous State.—M. Ponsot.—Two bodies, A and B, at a temperature T, are allowed to interact, giving rise to other bodies, for example M and N. The author examines such a reaction, choosing suitable bodies. Two systems are formed, one consisting of the bodies A and B, the other of the bodies M and N, in each case the solid bodies being accompanied by a mixture of their vapours. He finds that the heat brought into play by the total reaction of one body in a solid state, and supporting a pressure produced by the tension of the vapours it emits and the heat emitted during the total reaction, and under the constant volume of the same bodies when in the gaseous state, tends towards the same value at absolute zero.

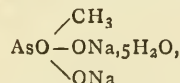
Heat of Solution of Solid and Liquid Ammonia at about -75° , and Latent Heat of Fusion of Solid Ammonia.—G. Massol.—The latent heat of fusion of ammonia has never been determined experimentally, but this constant is necessary if the heats of formation of the ammonia salts are to be compared with those of other alkaline salts, all the bodies being taken under the same initial

conditions. The method adopted by the author for finding this constant consists in dissolving in water in a calorimeter (1) liquid ammonia at -75° , i. e., at the temperature of solidification, (2) solid ammonia taken at a temperature as near as possible to -75° , the fusion temperature. The algebraic difference between the numbers obtained from these two thermic reactions gives the required constant, with a slight error, on account of the impossibility of obtaining the body in the two states exactly at the same temperature. The mean value obtained is -0.068 cal. for solid ammonia and $+1.77$ cal. for liquid ammonia. From these the number -1.838 cal., the molecular latent heat of fusion, can be obtained.

Volumetric Estimation of Thallium.—V. Thomas.—The author employs a modification of Feit's method for estimating thallium volumetrically. A thallic salt is treated with potassium iodide, and a greenish black precipitate is obtained. This may be considered as a mixture of thallic iodide and iodine, resulting from the decomposition of an unstable triiodide, $\text{TI}_2 = \text{THI} + \text{I}_2$. To estimate thallium volumetrically the solution should contain the metal in the form of thallic sulphate, and the transformation into thallic sulphate is absolutely necessary in the case of thallium existing in the liquid in the form of a halogen salt. Excess of potassium iodide is added, and enough arsenious solution to produce a pure yellow precipitate of thallic iodide. This is filtered, and to a portion of the filtrate excess of arsenious acid is added.

Acid and Basic Sulphates of Neodymium and Praseodymium.—Camille Matignon.—The author announces the existence of the new salts $\text{Nd}(\text{SO}_4\text{H})_3$, $\text{Pr}(\text{SO}_4\text{H})_3$, $(\text{NdO})_2\text{SO}_4$, $(\text{PrO})_2\text{SO}_4$, and examines certain of their properties.

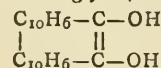
Alkalimetric Estimation of Disodic Methylarsinate or Arrhenal.—A. Astruc.—The author finds a simple and rapid method of estimating disodic methylarsinate, based on its alkaline reaction. The methylarsinate when analysed is found to correspond to the formula—



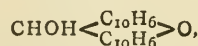
the theoretical percentage of water being 32.84 and of arsenic 27.37. A standard solution of this substance is titrated against a half decinormal solution of sulphuric acid, and the results obtained are satisfactory.

Some Derivatives of Arabinose.—G. Chavanne.—The author examines a sugar containing five carbon atoms, arabinose. This he prepares quite pure and in considerable quantity in order to obtain its oxidation products. By employing Kenig and Knorr's method he obtains an acetochlorarabinose and an acetobromoarabinose in a pure state.

The Supposed Binaphthaleneglycol.—R. Fosse.—In a preceding research the author showed that several bodies formed during the action of chloroform on the β -naphthol did not possess the constitution attributed to them. He now shows that the substance known under the name of binaphthalene glycol, with constitution—



is in reality dinaphthoxanthidrol, and has the constitution—



Similarly all the derivatives of this supposed dinaphthylene-glycol are really the corresponding derivatives of xanthidrol.

Pseudo-acids.—P. Th. Muller.—If RH represents the formula of an acid, its neutralisation by soda is expressed by the equation $\text{RH} + \text{NaOH} = \text{RNa} + \text{H}_2\text{O}$, and by ap-

plying the rule of mixtures for systems in solution, the molecular refraction may be expressed as follows:—

ref. RNa—ref. RH=ref. NaOH—ref. H₂O=K (constant).

The value of this constant is comprised between 1.5 and 1.6. Such reasoning necessarily supposes that the radicle R has the same structure in the acid and in the soda-salt. If this is not the case values for K differing from 1.55 should be obtained. The author establishes values for K between 3.5 and 4 for a certain number of isonitroso-compounds of the fatty series, oximidocyanacetic and isonitrosomalonic ethers, isonitrosoacetone, isonitrosocamphor, &c. Such belong to the category of substances which Hantzsch calls the pseudo-acids, substances whose constitution varies when they pass to the state of the neutral salts. The author intends to publish details of his research on this subject.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxv., Nos. 16—17.

Action of Hydrogen on Sulphide of Mercury.—H. Pélabon.—(See p. 172).

Action of Mercuric Oxide on Aqueous Solutions of Metallic Salts.—A. Mailhe.—Already noticed.

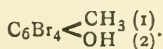
A New Crystallised Salicylate of Bismuth.—P. Thibault.—Already inserted in full.

Acidimetry of Phosphoric Acid by means of Barrya Water.—J. Cavalier.—Already inserted in full.

Action of Fuming Nitric Acid on Dimethylacrylate of Ethyl.—L. Bouveault and A. Wahl.—When dimethylacrylate of ethyl is poured into fuming nitric acid the mixture becomes strongly heated, and should be kept cool; on adding water a heavy oily liquid separates out, this is nitrodimehylacrylate of ethyl. The author describes in full the details of its preparation. When purified by re-distillation it consists of a very bright yellow liquid with a disagreeable odour. It is insoluble in water and dilute acids, insoluble in cold caustic alkalis; it dissolves, however, on heating or after prolonged contact in the cold, but not without decomposition. Its potassium salt, in which a molecule of hydrogen is replaced by one of potassium, gives coloured precipitates with the metallic salts.

Constitution of the α - and β -Nitrodimehylacrylic Ethers.—L. Bouveault and A. Wahl.—A long paper not suitable for abstraction.

Action of Bromine on Carvacrol in the presence of Bromide of Aluminium.—F. Bodroux.—Five grms. of carvacrol are poured, drop by drop, into 100 grms. of cold bromine containing 1 per cent of aluminium in solution. The reaction is energetic, and torrents of hydrobromic acid are given off. After six hours the excess of bromine was driven off by evaporation, and, as a result of the operation, a solid white mass was obtained, impregnated with a gummy substance, which, however, could be removed by washing with a little cold alcohol. This white product is soluble in warm dilute alcohol, and more so in chloroform, and on cooling deposits long, silky, white needles, fusible without decomposition at 208°. Its physical properties and its analysis show that the body obtained is tetrabromorthocresol—

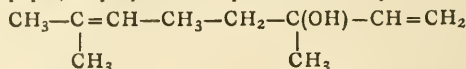


Some Iodised, Etherial, Phenylc Derivatives.—P. Brenans.—Already noticed.

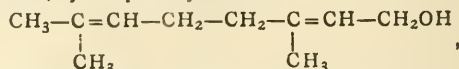
Examination of a New Class of Organic Compounds; Cyclic Isonitriles and Nitriles.—A. Sabanejeff and M. Prosin.—After describing the method of preparing these new compounds, the authors conclude that these isonitriles and nitriles are cyclic compounds of which the ring consists of several atoms of carbon and nitrogen in which the hydrocarbon group could easily pass from the

nitrogen to the carbon, and *vice versa*. The isonitriles and nitriles at present known represent the most simple case only, and are in the same relation to the cyclic isonitriles that ethylene is to the polymethylenic hydrocarbides.

The Constitution of Licareol (Linalol).—Ph. Barbier.—For various reasons which the author fully explains in this paper, he proposes to replace the tertiary formula—



which has been attributed to licareol, but which is really myrcenol, by the primary formula—



which is common to both licareol and lemonol, and to consider these two alcohols as stereo-chemical isomers.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Messrs. W. A. Bailey, J. M. Barr, C. W. Darley, W. E. L. Gaine, Carl Hentschel, J. C. Inglis, G. Northcroft, H. C. Plimmer, F. E. Robertson, and G. A. Wilson were elected Members. The special thanks of the Members were returned to Dr. Francis Elgar, F.R.S., for a donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

Hydrated Thiocyanate of Cobalt.—H. S. Kournakof.—By slowly evaporating a solution of a mixture of equivalent parts of CoSO₄ and Ba(CNS)₂, we obtain the hydrate Co(CNS)₂·3H₂O, crystallised in large, almost black plates belonging to the rhombic system, and which transmit a reddish-violet light through a very slight thickness. This hydrate effloresces in the air, and gives a yellowish-brown anhydrous salt. This latter is obtained crystallised in granular crusts by evaporating the solution on the water-bath. No salts are obtained with colours intermediate between violet and yellow, which seems to indicate that there is no intermediate hydrate.—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 354.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Society of Arts, 8. (Cantor Lectures). "Glass for Optical Instruments," by Richard T. Glazebrook, M.A., D.Sc., F.R.S.

TUESDAY, 15th.—Royal Institution, 3. "Recent Methods and Results in Biological Inquiry," by Allen Macfadyen, M.D., B.Sc., Fullerian Professor of Physiology, R.I.

WEDNESDAY, 16th.—Microscopical, 7.30. Exhibition of Pond Life. Society of Arts, 8. "Photography as Applied to Architectural Measurement and Surveying," by J. Bridges Lee, M.A.

THURSDAY, 17th.—Royal Institution, 3. "The Oxygen Group of Elements," by Prof. Dewar, M.A., LL.D., D.Sc., F.R.S., Fullerian Professor of Chemistry, R.I. Society of Arts, 4.30. "Recent Developments in Punjab Irrigation," by Sidney Preston, C.I.E.

Chemical, 8. "Oxonium Salts of Fluoram and its Derivatives," by J. T. Hewitt and J. N. Tervet. "The Influence of certain Acidic Oxides on the Specific Rotations of Lactic Acid and Potassium Lactate," by G. G. Henderson and D. Prentice. "The Amounts of Nitrogen as Ammonia and as Nitric Acid, and as Chlorine in the Rain-water collected at Rothamsted" and "The Amounts of Nitrogen as Nitrates and Chlorine in the Drainage through Uncropped and Unmanured Land," by N. H. J. Miller.

FRIDAY, 18th.—Royal Institution, 9. "The Autocar," by Sir John H. A. Macdonald, K.C.B., LL.D., F.R.S., M.Inst.E.E.

SATURDAY, 19th.—Royal Institution, 3. "British National Song" (with Musical Illustrations), by William H. Cummings, Mus.D. (Dub.), F.S.A., Hon K.A.M., Principal of the Guildhall School of Music.

THE CHEMICAL NEWS.

VOL. LXXXV., No. 2212.

THE COMPOSITION OF THE CANARY-YELLOW ARSENITE OF SILVER.

By J. ALFRED WANKLYN,
Corresponding Member of the Royal Bavarian Academy of Sciences.

THE canary-yellow arsenite of silver which every school-boy knows, and which is described in chemical text-books as "the tetrargentite salt, $2\text{Ag}_2\text{O} \cdot \text{As}_2\text{O}_3$," has been recently analysed in my laboratory. The result of the analysis has astonished me, and is certainly interesting.

The following are the details and the figures of the analysis:—

The arsenite of silver, as is well known, is produced when the gas from the Marsh's apparatus is led into solution of nitrate of silver. It separates from the filtered solution (the reduced silver having been left on the filter-paper) on the cautious addition of dilute ammonia to the filtered solution.

A quantity of the arsenite of silver prepared in that manner was washed and dried in the water-bath and analysed.

1.0135 grms. gave 0.966 gm. of AgCl and 0.277 gm. of As_2S_3 . The formula $3\text{Ag}_2\text{O} \cdot \text{As}_2\text{O}_3$ requires—

	Calculated.		Found.
$\text{Ag}_2 \dots$	648	72.48	71.73
$\text{As}_2 \dots$	150	16.78	16.66
$\text{O}_6 \dots$	96	10.74	—
	894	100.00	

The formula was confirmed by a synthetical experiment. A weighed quantity of As_2O_3 was dissolved in water, and an insufficient quantity of ammonia added, and then the observation was made that, on mixing with this solution a known quantity of nitrate of silver (excess of nitrate of silver being taken), the solution became powerfully acid during the precipitation of the yellow arsenite of silver. Dilute ammonia was then carefully added so as just to saturate the acid, and the resulting canary-yellow arsenite of silver was separated by filtration, washed, slightly pressed, dried at 212°F ., and weighed. The theoretical figures were experimentally obtained.

It is noteworthy that, in this experiment, the yellow colour of the precipitate was *not* lost on drying.

The Laboratory, New Malden, Surrey,
April 12, 1902.

ON MINERALS OCCURRING IN AUSTRALIAN BAT GUANO.

By R. W. EMERSON MACIVOR, F.I.C., &c.,
Formerly Assistant Professor of Chemistry, Anderson's College,
Glasgow; Consulting Chemist to the Royal Agricultural
Society of Victoria, Australia; &c.

SOME years ago I contributed a paper to the *CHEMICAL NEWS* (vol. lv., p. 215), in which I described the bat guano which forms extensive deposits in certain basaltic caves in the vicinity of Skipton, 30 miles south-west of Ballarat, and also gave an account of a number of interesting and well-defined minerals which occur in it. I propose in this communication to supplement the statements I then made by some new facts, particularly in respect to the two new magnesium-ammonium phosphates which I had named Dittmarite and Muellerite respectively, but which at the time I had not fully examined.

Struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, previously a rare mineral, occurs in great abundance in the moist depths of the guano, but rarely in the upper or drier portion of the deposits. It is sometimes associated with beautifully defined triclinic crystals of the more complex hydrous ammonium-magnesium phosphate, $\text{Mg}_2\text{H}_2(\text{PO}_4)_2 \cdot \text{MgH}_2(\text{NH}_4)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. Indeed, as stated in my earlier paper, the crystals of the latter are occasionally found adhering to those of the struvite in such a way as almost to suggest that they had grown out of the latter. But hannayite, the hydrous magnesium hydrogen phosphate, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, to which I gave the name newberyite, and the other well-defined minerals hereafter described, occur most abundantly in the seemingly older—or, at all events, drier—parts of the deposits containing the white indistinctly crystalline nodules of what appears to be altered struvite, and which approximate in composition to the normal tri-basic magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$. I may mention, in passing, that the aqueous extract of the guano contains, among many other salts, sodium-ammonium-hydrogen phosphate, $\text{NaNH}_4\text{HPO}_4$, which I succeeded in separating in a pure state by repeated crystallisations.

The crystallographic features of struvite, hannayite, and newberyite were years ago minutely examined and described by G. vom Rath, to whom I sent, through the late Prof. Ulrich, some representative specimens of each mineral (*Ber. Nied. Ges.*, p. 11, January 7th, 1878; and January 13th, 1879; also Dana's "A Treatise on Mineralogy," p. 832). I may take this opportunity of correcting a slight—but to me not altogether unimportant—error in connection with the discovery of hannayite into which vom Rath was led by a misstatement made in writing to him by Professor Ulrich, and which is repeated in Dana's great work of reference in a manner that reflects somewhat upon myself as a mineralogical chemist. The mineral is described as having been "discovered by MacIvor, of Melbourne, . . . and recognised as new by Ulrich, as stated in a letter to vom Rath." Now the facts of the case were that, by the time Ulrich came to my laboratory to obtain the specimens for Professor vom Rath, I had not only repeatedly analysed the mineral and by other means identified it as new, but had actually named it after my old friend and early associate Mr. J. B. Hannay. Ulrich had nothing whatever to do with its identification as a new species.

The following are some later analyses of—(A) struvite, (B) hannayite, and (C) newberyite from Skipton Guano:—

	(A).		(B).		(C).	
	Found.	Theory.	Found.	Theory.	Found.	Theory.
$\text{H}_2\text{O} \dots$	44.09	44.03	28.51	28.69	36.31	36.21
$\text{MgO}^* \dots$	16.51	16.38	18.76	18.87	22.96	22.99
$(\text{NH}_4)_2\text{O} \dots$	10.58	10.61	8.10	8.18	—	—
$\text{P}_2\text{O}_5 \dots$	28.82	28.98	44.63	44.26	40.73	40.80
	100.00	100.00	100.00	100.00	100.00	100.00

* Including equivalent MgO for FeO and MnO present in the three minerals:—(A). FeO , 0.81; MnO , 0.16. (B). FeO , 0.310; MnO , 0.087. (C). FeO , 0.85; MnO , 0.021.

Dittmarite is met with in the form of small rhombic transparent crystals, which do not readily lose water on lengthened exposure to the atmosphere, but give up much of their water of crystallisation and lose transparency on being maintained for a time at $100-105^\circ$. On ignition, it yields magnesium pyrophosphate. Its composition indicates the somewhat extraordinary formula $\text{MgNH}_4\text{PO}_4 \cdot 2\text{Mg}_2\text{H}_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$.

	Found.		Theory.
$\text{H}_2\text{O} \dots$	23.42	23.65	
$\text{MgO}^* \dots$	26.13	26.28	
$(\text{NH}_4)_2\text{O} \dots$	3.94	3.42	
$\text{P}_2\text{O}_5 \dots$	46.51	46.65	
	100.00	100.00	

* Including MgO equivalent to 0.38 FeO and 0.08 MnO .

This interesting mineral I named in honour of my old and esteemed principal, the late Professor W. Dittmar, F.R.S.

Muellerite is yet another remarkable ammonium-magnesium phosphate found here and there sparsely distributed in the older and moderately moist (about 18 to 25 per cent H_2O) guano deposits. It occurs in small flat crystals of somewhat indistinct character, and which are with difficulty freed from adhering and locked up guano. However, after the exercise of considerable patience, I succeeded in separating some fairly clean crystals, which on drying at $100^\circ C.$ for two hours did not lose water of crystallisation, but at $120^\circ C.$ commence to lose weight. On strong ignition the mineral left magnesium metaphosphate, $Mg(PO_3)_2$, and, on analysis, gave numbers indicating the formula $Mg(NH_4)_2H_2(PO_4)_2 + 4H_2O$:—

	Found.	Theory.
H_2O	27.55	27.77
MgO^*	12.42	12.35
$(NH_4)_2O$	16.15	16.05
P_2O_5	43.88	43.83
	100.00	100.00

* Including MgO equivalent to 0.20 FeO and 0.05 MnO .

This mineral I called *Muellerite*, in compliment to the illustrious Australian scientist, the late Baron Sir Ferdinand von Mueller, K.C.M.G., F.R.S., with whom I was much associated during my eleven years' work at the Antipodes.

The chalk-like white nodules, incidentally referred to in my earlier paper and also in this note as being "altered" struvite, and which are found abundantly distributed throughout the mass of some of the drier guano deposits, appear to consist largely of imperfectly crystalline tribasic magnesium phosphate, $Mg_3(PO_4)_2$. However, neither the chemical nor crystallographic data at present in hand will permit of my stating that this nodular material is really a distinct mineral species, but I hope soon to have an opportunity of settling the point.

In order to show the general composition of the "drier" guano deposits, in which hannayite, newberyite, dittmarite, muellerite, and the nodular mineral most usually occur, I quote the following analysis :—

Water	19.80
Organic matter*	52.83
Ash†	27.37
	100.00

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METHOD FOR THE ESTIMATION OF THE TOTAL ALKALI, THE FREE ALKALI, AND THE CARBONATED ALKALI IN SOAPS.

By R. HENRIQUES and O. MEYER.

ONE single process can be used for determining the free and carbonated alkalis, which are usually present in small quantities only (2 to 5 per cent), at the same time as the alkalis of the fatty acids, in most household soaps. This process is based on the use of absolute alcohol, which dissolves the alkaline soaps and the free alkali, while

* Nitrogen (nearly all nitrates), 2.98.

† The ash contained—

Silica (and insol. in HCl r.r.t. sp. gr.) ..	3.65	K_2O	1.79
$Fe_2O_3 \cdot Al_2O_3$	5.23	P_2O_5	5.38
CaO	2.00	SO_3	1.57
MgO	0.98	SiO_2 (sol.)	1.06
Na_2O	2.93	CO_2	2.00

The ash contained only a mere trace of manganese—a remarkable fact when we note the more than appreciable quantity of that substance contained in each of the minerals occurring in the guano.

apparently leaving the carbonated alkali intact. Unfortunately, this latter also is fairly soluble in absolute alcohol, and, further, the large percentage of water present in all soaps does not allow of the direct application of the method in question to soap. It is indispensable to thoroughly dry the soap under examination, and many other difficulties have also to be surmounted. Again, and this is the weakest point of the method, the free alkali becomes partially carbonated, which leads to results altogether erroneous.

The small apparatus, of which the following is a description, enables us to determine in a very simple manner and with great accuracy, not only the free and carbonated alkali, but also a certain number of other constants, in such a way that a complete analysis of a soap can be effected very rapidly and without difficulty. It consists of an Erlenmeyer matras of about 400 c.c. capacity, fitted with a cork pierced with three holes. One of these holes takes a small funnel, of about 100 c.c., furnished with a tap, the others take respectively the inlet and outlet air tubes. The air passing through the inlet tube is previously freed from its carbonic acid by being passed through a wash-bottle filled with strong soda-lye; the air is next passed through a drying flask filled with concentrated sulphuric acid. This apparatus is completed by a chloride of calcium tube, and a tared potash tube to retain the carbonic anhydride resulting from the decomposition of the soap. Finally, a 3 litre aspirator fitted with a syphon and pinchcock completes the apparatus.

The following is the method of working we adopted :—From 5 to 10 grms. of the soap are placed in the Erlenmeyer matras; this is dissolved in about 100 c.c. of warm water, and allowed to cool; the matras is then connected with the rest of the apparatus, and after making sure that the whole system is air-tight, dilute hydrochloric acid is run in through the funnel. Some excess of acid may be used when only the carbonated alkali is to be estimated; but if we also wish to determine the proportion of free alkali present, it is necessary to use an accurately measured volume of demi-normal acid. In all cases, however, this volume must be more than that actually needed for the complete decomposition of the soap. If the sample taken is 5 to 10 grms., 50 c.c. of demi-normal acid will suffice. The acid is run into the soapy liquor, the funnel rinsed, the tap closed, and a slow current of air allowed to pass through the apparatus. The matras is then heated gently, and it is the intensity of the heat which governs the regularity of the decomposition of the soap. The flame of the Bunsen burner should be regulated to about the size of a nut. After from thirty to forty-five minutes, provided the decomposition has proceeded regularly, the fatty acids ought to collect in a clear melted layer, and the whole of the liquid should be almost boiling.

As soon as the first drops of condensed steam reach the outlet tube the flame is removed, and the current of air allowed to pass for thirty or sixty more minutes, to completely drive out all the carbonic anhydride and bring it to the potash apparatus. It then suffices to weigh the latter to determine the weight of carbonate.

If, at the same time, we wish to determine the free alkali, we must continue in the following manner :—After absorbing the whole of the carbonic anhydride, the apparatus is disconnected, the funnel is well washed, the wash-water being allowed to run into the soapy liquor, which is once more brought almost to the boiling-point, and we continue the determination by *Hehner's method*; that is to say, the insoluble fatty acids are collected on a filter, and washed with warm water until the washings are no longer acid. The total aqueous solution is then titrated with demi-normal soda, taking into account the amount of demi-normal hydrochloric acid used for the decomposition of the soap.

In this manner we arrive at the *total alkalinity*.

The insoluble fatty acids are now dissolved in warm alcohol, and the alcoholic solution obtained is titrated

with an alcoholic solution of demi-normal soda, which gives the alkali combined with the fatty acids.

Let us call *a* the total alkalinity, *b* the alkali due to the carbonic anhydride, and *c* the alkali due to the fatty acids; the whole expressed as NaHO or KHO, in grms. or parts per cent of soap, it is evident that the value *a b c* represents the free alkali; the silicates and borates being neglected in the case with which we are dealing.

The results obtained by the method described are very exact, and a complete analysis can be made in two or three hours. Further, it allows of the calculation or determination of other constants at the same time. The neutralised alcoholic solution of the fatty acids gives the proportion of *pure soap*, the most important indication in the valuation of a soap.

It is sufficient to evaporate this alcoholic solution, then to weigh the residue obtained, and to deduct from it the proportion of alkalis found, to get the percentage of fatty acids, and we should know at the same time the acid value and the mean molecular weight of these latter bodies.

We may add, however, that in some cases our process does not give results free from all suspicion. When we have to deal with soaps containing fatty acids soluble in warm water, Hehner's method is not sufficient, the total acidity may still be estimated, and that, either by means of a Huggenberg burette, or with an ordinary separating funnel.

The soap is decomposed by means of a weighed quantity of etherised acid, the acid-lye is removed, and by neutralising the etherised solution by means of a titrated alkaline-lye, the *pure soap* is obtained, which allows of the determination of the proportion of *total fatty acids*.—*Zeit. f. Angew. Ch.*, 1900, p. 785.

REMARKS ON COMMERCIAL PEROXIDE OF HYDROGEN.

By. G. ARTH.

It is advisable to call the attention of those who buy and use peroxide of hydrogen to some peculiarities regarding the analysis of this product.

I. It has been stated recently that some manufacturers add to their peroxide of hydrogen a certain quantity of oxalic acid. As in practice the richness of the product is always determined volumetrically by means of permanganate of potash in the presence of an excess of sulphuric acid, this addition would have the effect of decolorising a larger quantity of the indicator than that corresponding to the actual amount of H_2O_2 , and thus augmenting the value in a fictitious manner. Further, this practice is unexpected *à priori*, as it is well known that oxalic acid and peroxide of hydrogen decompose each other reciprocally. Further on I shall lay stress on this point.

The method of analysis recommended to purchasers to detect this falsification is as follows:—To 100 or 200 c.c. of peroxide of hydrogen in a large foot-glass, we gradually add the equivalent volume of distilled water and pure ammonia until the reaction is distinctly alkaline (in practice several cubic centimetres of concentrated ammonia), then an excess of a neutral solution of chloride of calcium. If there is any oxalic acid or alkaline oxalate present in the peroxide of hydrogen, we obtain, after stirring the liquid vigorously, a granular crystalline precipitate of oxalate of lime, which eventually adheres strongly to the sides of the glass. But this precipitate of oxalate of lime may be mixed with a more or less considerable quantity of sulphate or phosphate of lime, and thus not have this characteristic appearance. In this case the precipitate is filtered and washed with distilled water containing ammonia, until the wash-waters, acidulated with sulphuric acid, no longer decompose permanganate of potash. The precipitate is

then treated with very dilute warm sulphuric acid, and, in the limpid solution, oxalic acid is tested for qualitatively with permanganate which is decolorised, or even estimated with the help of the same reagent, after diluting the whole to a known volume, and taking an aliquot part.

I have had occasion to examine a large number of samples of commercial peroxide of hydrogen, and in one sample, by means of the above process, I detected the presence of a fairly large proportion of oxalic acid. A closer study of this question has shown me, however, that this method of analysis is inexact, and may lead to the apparent detection of oxalic acid where it does not exist. The following is what I have observed with regard to this matter:—

(a). When we wash the precipitate obtained by the ammonia and chloride of lime, we find that the washings, acidulated with pure sulphuric acid, are never entirely without action on the indicator; they always decolorise it a little—not much it is true, but still they do decolorise it, no matter how prolonged the washing has been. Thus the precipitate is dissolved or slightly decomposed on contact with ammoniacal water, a property which is not possessed by oxalate of lime. Further, if the washing is done with distilled water only, the filtrate is always slightly alkaline, even when Nessler's reagent no longer gives any reaction.

(b). If we now examine the very dilute sulphuric solution in which the precipitate is dissolved, we first of all notice that it decolorises the permanganate *immediately in the cold*; this does not occur with oxalic acid.

The acid solution neutralised with ammonia remains limpid for an indefinite time; if it contained oxalic acid and sulphate of lime in solution, oxalate of lime should be re formed (this is exactly what does happen if we add a trace of oxalic acid after neutralisation).

This acid solution, treated with permanganate of potassium, gives off pure oxygen free from carbonic acid, a compound which would not fail to be evolved in the presence of oxalic acid.

Finally, this sulphuric solution gives the reactions of peroxide of hydrogen very distinctly (with chromic acid and ether, &c.).

I may add that the calcic precipitate (a so-called mixture of oxalate with a little phosphate of lime), which is at first brilliant and transparent, effloresces and becomes opaque on contact with dry air; after drying at 100° , or *in vacuo*, it has a strong alkalinity which cannot be accounted for by a mixture of oxalate and phosphate of lime.

We are thus brought to the conclusion that this alkaline precipitate, which is slightly soluble in water and capable of reproducing peroxide of hydrogen under the action of dilute sulphuric acid, is nothing other than hydrated binoxide of calcium, and not oxalate of lime as supposed. The error is excusable, as we should not have expected this binoxide to be precipitated under these conditions. I further propose to return to this method for the production of binoxide of lime, which is obtained so easily with pure distilled peroxide of hydrogen. The precipitate answers to the formula $CaO_2 \cdot 8H_2O$, which is already known.

I have further verified the fact that the suspected peroxide of hydrogen, which gave 8.28 volumes by the permanganate titration, gave 8.19 volumes when decomposed by binoxide of manganese and dilute sulphuric acid; the gas evolved is entirely free from carbonic acid.

II. On the occasion of this examination I was anxious to note the effect of the addition of a certain quantity of oxalic acid to ordinary commercial peroxide of hydrogen. For this purpose I made use of a very pure sample of peroxide manufactured by Messrs. Gignoux, of Lyons. At the time of the experiment this substance titrated 10.70 volumes; a portion of it was treated with crystallised oxalic acid to the extent of 20 grms. per litre, and another portion with 10 grms. per litre. These solutions were all titrated together:—

	With 20 grms. per litre.	With 10 grms. per litre.
March 13 ..	12.20 volumes	11.30 volumes
" 21 ..	10.19 "	10.44 "
" 28 ..	9.50 "	10.11 "
April 5 ..	9.15 "	9.92 "

It is evident that the decomposition is rapid, especially at first; after a week only it is below its original strength. The peroxide treated with 20 grms. of oxalic acid continuously gives off minute bubbles of gas, principally during the first few days; it could not be transported, therefore, in corked vessels. The use of alkaline oxalates instead of the free acid would be easily detected by determining the weight of the residue left after drying at 100°, and it is sufficiently improbable that a cheap compound could be added, in which the oxalic acid would be sufficiently imitated, and which would resist the action of the peroxide of hydrogen, and only reveal its presence in the titration with permanganate, or even after the addition of a strong dose of caustic ammonia.

III. It now remains to make a few remarks on the manner in which certain manufacturers effect the valuation of the volume of oxygen which peroxide of hydrogen can evolve. They make the titration by means of a N/50 solution of permanganate of potassium, thus containing 3.163 grms. of this salt per litre. They operate on 2 c.c. of peroxide of hydrogen, and the number of c.c. of permanganate used, divided by 3, is taken as the titration value of the product; that is to say, to indicate the number of volumes of oxygen which 1 volume of the liquid will give.

Now, this number in reality corresponds with *nothing*. Theoretically, it requires a liquor containing 5.659 grms. of permanganate per litre when operating on 1 c.c. of peroxide of hydrogen, for the volume of the reagent used to indicate, directly, the available volume of oxygen (measured at 0° and 760 m.m.). The difference between the results given by the two solutions is not negligible; in fact, the relation between this *arbitrary* and *inexact* volume of oxygen and the *real* volume is 1/0.838; a peroxide described as 10 volumes thus only gives in reality 8.38 volumes, the difference being 19.3 per cent of the real volume.

It has been impossible to find out the reason for this method of operating. In the trade it is the rule to suppress calculations whenever possible, and not to introduce useless ones, a procedure which would be necessary if we wish to use *correctly* N/50 solution; further, it is no more difficult to prepare a solution titrating 5.659 grms. per litre than one containing 3.163 grms.

We can only hope to see this irrational practice disappear, it being a source of difficulties and disputes. Users who buy peroxide of hydrogen could easily bring about this result by insisting that manufacturers should give the *real* titration value of the product they supply.—*Moniteur Scientifique*, Series 4, vol. xv., No. 715.

THE ESTIMATION OF TUNGSTEN IN ORES.

By F. BULLNHEIMER.

THE analysis of impure or undressed tungsten ores is very tedious, principally on account of the presence of phosphorus and arsenic (due respectively to the apatite and arsenical pyrites which accompany the ores), which form double compounds with the tungstic acid, and make the exact precipitation of pure tungsten compounds impossible.

The treatment with aqua regia is tiresome, and fusion with cyanide and soda is unsatisfactory.

The author recommends a preliminary fusion with peroxide of sodium and a little caustic soda in a nickel crucible; the soda increases the fluidity of the mixture and enables the same crucible to be used for about twenty assays.

The mixture may contain stannate, arseniate, molybdate, phosphate, and silicate of sodium, besides the tungstate, as well as other impurities which have no action, and should therefore be eliminated.

One to 2 grms. of the ore are mixed in a nickel crucible with 4 grms. of peroxide of sodium and 3 grms. of caustic soda; this caustic soda, in one single lump, should be placed at the bottom of the crucible, which is gently heated over a Bunsen burner until the whole mass is softened; the flame is then increased until the whole mass becomes completely fluid and the bottom of the crucible commences to look red. The wolfram is quickly and completely dissolved by this method, while the tin-ore remains partly unchanged.

After solidification, the still hot crucible is placed in a vessel containing water, and the solution obtained is transferred to a flask of about 250 c.c. capacity.

If any manganate is present, the green colour can be made to disappear by means of peroxide of hydrogen.

Once cool, the flask is filled with water up to the mark, and half the solution is filtered.

Twenty grms. of nitrate of ammonium are then added (this suffices to convert the whole of the caustic soda into nitrate, giving at the same time a marked excess of free ammonia). After solution, the mixture is allowed to stand so as to precipitate the silicic and stannic acids; the necessary amount of nitrate of magnesium is then added in small quantities with continual stirring to precipitate the arsenic and phosphoric acids which may be present. The salt of magnesia should not be added until the silicic and stannic acids have been removed, or else tungsten would be found in the precipitate.

It is necessary to use nitrates of ammonia and magnesia, as the chlorides or sulphates would interfere with the subsequent use of mercurous nitrate.

After standing for from six to twelve hours the precipitate is filtered, then washed, first with ammonia, and then with water. The filtrate is made slightly acid with nitric acid, and, after cooling, if the acid has caused any appreciable rise of temperature, 20 or 30 c.c. of mercurous nitrate are added. To prepare this solution, 200 grms. of HgNO₃ are gently heated with 20 c.c. of nitric acid and a little water; this is then diluted up to 1 litre, and mercury added. Some hours later, ammonia is added until the solution is only faintly acid; the whole is then allowed to stand until the supernatant liquid becomes quite limpid.

The precipitate is then filtered and well washed with water containing mercurous nitrate.

If the above instructions are carefully carried out, the filtering as well as the washing can be done without any trouble.

The precipitate is then calcined, first over a Bunsen burner and then before the blowpipe until the weight is constant.

When there is much molybdenum present, which, however, is rarely the case, some time may elapse before this metal is entirely volatilised, and the weight no longer changes. The end of the operation can be hastened if, after having first heated strongly, we add a little chloride of ammonium. The heat is then applied again strongly, first with the crucible covered, and afterwards with the cover off.—*Chem. Zeit.*, xxiv., 870.

Action of Halogenated Ethers on the Sulphocarbonic Compounds of the Secondary Amines.—Marcel Delepine.—The author describes a very simple method for the preparation of the bisubstituted azoic thiosulphocarbamic ethers. He then examines the chief properties of these ethers and their relative stability. By the same method he proposes to obtain the urethanes R.NH.CSSR' and NH₂.CSSR, whose fragility and ease of reaction contrasts with the resistance of the dithiourethanes.—*Comptes Rendus*, cxxxiv., No. 12.

THE BOILING-POINT CURVE FOR MIXTURES OF ETHYL ALCOHOL AND WATER.*

By WILLIAM A. NOYES and R. R. WARFEL.

It has long been known that it is impossible to obtain absolute alcohol from dilute alcohol by distillation. Some years ago Le Bel (*Comptes Rendus*, lxxxviii., 912) showed, also, that a 98 per cent alcohol could be separated by fractional distillation into an alcohol of 97.4 per cent (by volume), and a residue containing 99.5 per cent. While these facts demonstrate that the boiling-point of absolute alcohol must be higher than that of alcohol slightly diluted, no one, so far as we can learn, has proved this by means of a direct determination.

The determination of the boiling-point curve for alcohol-water by J. K. Haywood (*Journ. Phys. Chem.*, iii., 318), has come to our notice since reading the proof of this article. Haywood entirely overlooked the minimum point. His curve, from alcohol of 85 per cent down, agrees satisfactorily with ours.

The boiling-point apparatus of H. C. Jones (*Am. Chem. Journ.*, xix., 581) was used for the determinations. The tube of the condenser was sealed to the side tube of the apparatus, and was protected from the entrance of moisture at the top by means of a tube filled with calcium chloride. A small glass tube was inserted through the cork beside the thermometer, for the introduction of water or alcohol.

The alcohol used was rendered absolute by boiling twice with quicklime, the second time with the addition of a small amount of barium oxide. In distilling it, the first and last portions were rejected. The specific gravity of the alcohol indicated a strength of 99.98 per cent.

The boiling-points for alcohol from 100 per cent to 64 per cent were determined with a Beckmann thermometer graduated to 1/100°. Those from 64 per cent to 0 per cent were determined with a normal Green thermometer graduated in 0.1°. To determine the value of the degrees of the Beckmann thermometer the apparatus was connected with a large flask and a manometer, and the alcohol was boiled under diminished and also under increased pressure. In this way it was found that a difference of 1 m.m. in pressure caused, at atmospheric pressure, a change of 0.0333° in the boiling-point. Ramsay and Young's tables give 0.0339° for 1 m.m. (*Journ. Chem. Soc.*, xlvii., 640). The value of the degrees was accordingly taken as being sufficiently accurate for the present purpose.

To find the value of the Beckmann readings in terms of the true thermometer scale, pure water was placed in the apparatus, and it was connected with a large bottle and a manometer. The pressure was then reduced till the water boiled at about 80° of the true scale and a series of readings of thermometer, barometer, and manometer were taken. The barometer and manometer readings were corrected to 0° and by comparison with Regnault's tables for the vapour-pressure of water, the point on the true thermometer corresponding to the readings of the Beckmann thermometer was determined. From this value the boiling-point of absolute alcohol under a pressure of 760 m.m. is, as determined by us, 78.33°. The boiling-point calculated from the tables of Ramsay and Young (*loc. cit.*) is 78.30°. As Ramsay and Young doubtless had much more accurate means than we could command for measuring heights of manometer and barometer, we have based our tables on their value for the boiling-point, instead of our own.

The barometer used was of the syphon form. The scale was compared with a standard scale by means of a dividing engine before it was filled, and the necessary correction applied. It was filled by ourselves, the mercury

being boiled under diminished pressure during the filling.

In carrying out a series of determinations a weighed amount of alcohol or of water, or, in some cases of dilute alcohol, was put into the apparatus and the boiling-point determined. A weighed amount of water or alcohol was then added, and the determination repeated. Each time, the barometer and its temperature were also read. The results were then corrected to a basis of 760 m.m. by adding or subtracting 1/30° for each 1 m.m. difference in pressure. The nature of the readings will be apparent from the following illustration. In correcting the barometer readings a plus correction of 1 m.m. for error of scale is included.

SERIES 7.

Grm. of water added.	Barometer.	Temperature.	Barometer corrected to zero.	Beckmann readings.	Beckmann readings corrected to 760 m.m.	Per cent alcohol.
0.0000	737.6	19.5	736.13	2.948	3.744	99.98
0.2128	737.9	20.0	736.37	2.925	3.713	99.51
0.2440	737.95	20.0	736.42	2.907	3.693	98.97
0.1790	738.0	18.0	736.72	2.895	3.671	98.58
—	—	—	—	—	—	—
0.2900	743.5	17.5	742.28	3.089	3.680	92.42
0.2860	743.7	17.5	742.48	3.115	3.699	92.10

Started with 44.478 grms. of alcohol of 99.98 per cent.

Six series of experiments, made before the use of the apparatus had been sufficiently mastered, were rejected. Four series which gave fairly concordant results were used to obtain mean values for the range from alcohol of 100 per cent to 92 per cent. From these series the following values for each change of 1/2 per cent in the amount of water were calculated by interpolation:—

Per cent of alcohol.	7.	8.	10.	11.	Mean.	
100.0	3.745	3.738	3.756	3.759	3.750	0.030
99.5	3.714	3.708	3.727	3.730	3.720	0.027
99.0	3.695	3.680	3.700	3.698	3.693	0.021
98.5	3.669	3.655	3.687	3.678	3.672	0.017
98.0	3.653	3.639	3.674	3.654	3.655	0.016
97.5	3.638	3.625	3.658	3.634	3.639	0.008
97.0	3.620	3.619	3.651	3.632	3.631	0.004
96.5	3.624	3.612	3.643	3.629	3.627	0.003
96.0	3.626	3.613	3.633	3.625	3.624	0.002
95.5	3.627	3.613	3.634	3.632	3.626	0.001
95.0	3.625	3.611	3.638	3.633	3.627	0.009
94.5	3.636	3.623	3.647	3.639	3.636	0.009
94.0	3.635	3.630	3.660	3.655	3.645	0.016
93.5	3.653	3.644	3.678	3.668	3.661	0.016
93.0	3.672	3.656	3.698	3.682	3.677	0.014
92.5	3.679	3.667	3.713	3.705	3.691	0.018
92.0	3.694	3.685	3.728	3.728	3.709	

The remainder of the boiling-point curve possesses less interest, and it was not attempted to secure the same degree of accuracy. From alcohol of 92 per cent to 65 per cent two series of determinations were made and the Beckmann thermometer was used.

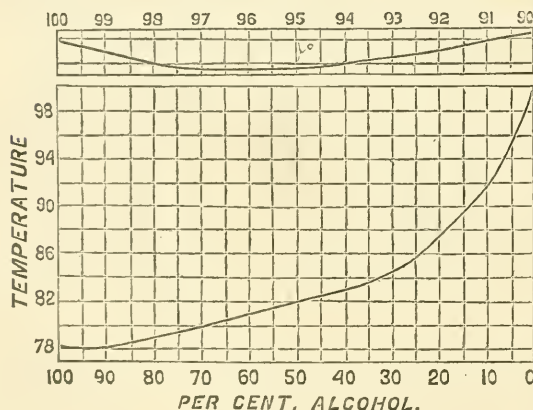
For alcohol from 65 per cent to 0 per cent, two series were made and the normal Green thermometer was used. As a part of the stem of the thermometer was outside of the apparatus, a stem correction from the tables of Rimbach was used (*Ber.*, xxii., 3075). The correction for the thermometer at 100° was determined in the apparatus with pure water, and the correction at 80° was determined by comparison with the Beckmann thermometer, whose value had been determined as described above. As the two corrections were different a table of corrections for intervening degrees was calculated on the supposition that the scale of the thermometer was uniform.

The final results of all the series are as follows:—

* An account of the work here described was presented to the Faculty of the Rose Polytechnic Institute as a thesis for the Degree of Bachelor of Science. From the *Journal of the American Chemical Society*, xliii., No. 7.

Per cent of alcohol.	Boiling-point.	Per cent of alcohol.	Boiling-point.
100.0	78.300	78.0	79.214
99.5	78.270	77.0	79.354
99.0	78.243	76.0	79.404
98.5	78.222	75.0	79.505
98.0	78.205	73.0	79.683
97.5	78.191	71.0	78.862
97.0	78.181	69.0	80.042
96.5	78.179	67.0	80.237
96.0	78.174	65.0	80.438
95.5	78.176	63.0	80.642
95.0	78.177	55.0	81.77
94.5	78.186	48.0	82.43
94.0	78.195	37.0	83.76
93.5	78.211	35.0	83.87
93.0	78.227	29.2	84.86
92.5	78.241	26.0	85.41
92.0	78.259	22.0	86.11
91.0	78.270	20.0	87.32
90.0	78.323	18.0	87.92
89.0	78.385	13.0	90.02
88.0	78.445	10.0	91.80
87.0	78.530	8.0	93.10
86.0	78.575	7.0	93.73
85.0	78.645	5.50	94.84
84.0	78.723	4.50	95.63
83.0	78.806	3.0	97.11
82.0	78.879	2.0	98.05
81.0	78.968	1.50	98.55
80.0	79.050	1.00	98.95
79.0	79.133	0.50	99.65

In the determination with small amounts of alcohol the readings of the thermometer were taken when the vapours first entered the condenser, as after boiling for a few minutes a relatively large proportion of the alcohol present would be found in the upper layers and in the condenser, and the thermometer under those conditions registered about 0.3 higher. It was shown by slow heating that the difference was not due to the lag of the thermometer.



An examination of the table and curve shows that the minimum boiling-point is for alcohol of 96 per cent by weight. This corresponds to 97.45 per cent on an enlarged scale. Le Bel (*loc. cit.*) gives the minimum as at 97 per cent (presumably by volume, though he does not make this statement). His method would tend to place the minimum too low, unless moisture was very carefully excluded.

In the accompanying figure the upper part gives the boiling-point curve for alcohol of 90 to 100 per cent on an enlarged scale. The lower portion of the figure gives the complete curve.

It will be seen that the curve is steeper on the side toward absolute alcohol than on the other side. Alcohol of 90.7 per cent has the same boiling-point as absolute

alcohol. An inspection of the curve also shows very clearly why it is easy to concentrate alcohol by distillation to a strength of 30 or 40 per cent by weight, while the further concentration is relatively difficult.

A NEW INVESTIGATION CONCERNING THE ATOMIC WEIGHT OF URANIUM.*

By THEODORE WILLIAM RICHARDS
and
BENJAMIN SHORES MERIGOLD.

(Continued from p. 178).

Preliminary Work upon the Preparation, Properties, and Methods of Analysis of some Uranium Compounds.

IN view of the well-known advantages of the halogen compounds for accurate analysis, when these compounds can be prepared and weighed in a state of purity—it seemed desirable to use a halogen compound as the basis of a determination of the atomic weight of uranium.

Of the four chlorides of uranium known to exist, none can be prepared in a state of purity that is beyond question. Green uranous chloride, UCl_3 , which results from passing dry chlorine over a mixture of uranium oxide and carbon at red heat, is easily converted to the pentachloride, UCl_5 , by further action of chlorine at high temperatures. There can be no positive evidence that the green chloride would not contain some of the pentachloride, and if the attempt is made to prepare the pentachloride from the green chloride, it is equally difficult to be sure that the conversion is complete. The trichloride, UCl_3 , is made by reducing the tetrachloride with hydrogen, and here again it is difficult to be sure that the tetrachloride is completely reduced. Uranyl chloride, UO_2Cl_2 , cannot be prepared in the dry state.

It is extremely probable, then, that any of the chlorides will contain larger or smaller quantities of a higher or lower chloride. It may be observed, in this connection, that Zimmermann used the chlorides in his vapour density determinations, and his analyses show good agreement. This does not show conclusively, however, that his material was free from small but fairly constant quantities of higher or lower chlorides as impurities.

On the other hand, bromine forms with uranium only three distinct compounds: the tribromide, UBr_3 ; uranous bromide, UBr_4 ; and the oxybromide, or uranyl compound, UO_2Br_2 . The tribromide can be produced only from the tetrabromide by the action of reducing agents. Uranyl bromide, UO_2Br_2 , has been certainly formed only in solution, resulting in hydrated crystals. It has never been definitely obtained in anhydrous form. Zimmermann made many attempts to form the pentabromide corresponding to the pentachloride, by passing bromine at high temperatures over sublimed uranous bromide. Every attempt gave negative results, showing that at temperatures up to the subliming point of uranous bromide higher bromides cannot exist. Since higher bromides are non-existent under the conditions prevailing in the formation of the tetrabromide, the objections to the use of the tetrachloride are not applicable in the case of uranous bromide. The investigations of Zimmermann (*Ann. der Chem.*, ccxvi., 3) have shown that the tetrabromide can be formed in an apparently definite state. It seemed probable, therefore, from the literature on the subject, that in uranous bromide we had a compound well suited to the purposes of our investigation.

The method of preparation followed at first was essentially that described by Zimmermann (*Ann. der Chem.*, ccxvi., 3). In an apparatus constructed wholly of glass, a mixture of dry nitrogen and bromine vapour was passed over a mixture of the green oxide of uranium,

* Contributions from the Chemical Laboratory of Harvard College from the *Proceedings of the American Academy of Arts and Sciences* xxxvii., No. 14.

U₃O₈, and pure carbon. The air was first thoroughly swept out of the apparatus by a current of nitrogen, and the oxide was heated to a high temperature. When the bromine vapour was passed in, uranous bromide formed, and sublimed in brilliant crystalline plates of a brownish colour. After cooling in a current of nitrogen, the sublimate was transferred to a weighing bottle. At this point, however, unexpected difficulties arose, owing to the rapid oxidation of the bromide. Uranous bromide is extremely deliquescent, and forms with water and oxygen the oxybromide, with liberation of hydrobromic acid. Consequently, when exposed to the moist air of the laboratory, even for the short time required for removing the sublimate from the combustion tube, the bromide loses its brilliant lustre, and assumes a dull, greenish yellow appearance, due to formation of the oxy-salt. If not protected from further action of moist air, the salt liquefies completely in a surprisingly short space of time.

In an attempt to change the coating of oxybromide back to the normal salt, recourse was had to the method which has been used successfully in many atomic weight investigations carried on in this laboratory. The salt was transferred to a platinum boat, and placed, with a weighing bottle of suitable size, in a glass bottling apparatus. (For a description of this apparatus see *Proc. Amer. Acad. Arts Sci.*, xxii., 59). A stream of dry hydrobromic acid gas was then passed over the bromide at a temperature just below the subliming point of the salt. This treatment, however, fails to restore the original brilliant appearance of the freshly sublimed bromide. The yellow colour of the oxybromide still remains. Apparently the oxybromide, once formed, cannot, by this method, be reduced to the normal uranous bromide.

In the previous investigations upon zinc, magnesium, nickel, and cobalt, in which this method of converting oxy-salts to the normal compounds has been used, the presence of even minute quantities of oxy-salt was made known by the opalescence of the solutions on account of the insolubility of these salts. With uranium, however, this method of detecting the presence of uranyl bromide cannot be used, for the oxybromide of uranium is even more soluble than uranous bromide.

The analysis of uranous bromide presents further difficulties. All uranous salts reduce silver nitrate. When a solution of silver nitrate, slightly in excess of the calculated amount, is added to a solution of uranous bromide, the silver bromide first precipitated is probably mixed with metallic silver; for if the silver bromide is filtered off, and the filtrate set aside, finely divided metallic silver soon separates. If a large excess of silver nitrate is added to the uranous bromide, a brilliant purple precipitate is obtained. It is possible that the precipitate may be a mixture of finely divided metallic silver and argentic bromide, or perhaps of normal argentic bromide and the long sought sub-bromide. Although this is an interesting phenomenon, it was not considered advisable to interrupt the research at this period for the length of time necessary for an investigation. The addition of nitric acid prevents the formation of this coloured precipitate, but owing to the danger of the loss of bromine, this is not an advisable expedient. Of course, it is possible to determine the bromine by first precipitating the uranium and adding silver nitrate to the filtrate, but this introduces a complexity of operations incompatible with the degree of accuracy requisite in an atomic weight investigation.

On account of these formidable difficulties in the preparation and analysis of pure uranous bromide, it was thought best to search for some compound which offered fewer obstacles. It will be seen that this search was vain, although it required many months.

In view of the great tendency of uranous bromide to oxidise under ordinary conditions, the use of uranyl bromide seemed to offer the simplest solution of the problem. Anhydrous uranyl bromide has never been prepared in a pure state. In the preparation of uranous bromide, if the nitrogen used contains a little oxygen, or

if traces of moisture are present, there is formed, in addition to the uranous bromide, a yellow powder, very different in appearance from the brown colour of finely divided uranous bromide. This powder has been assumed by various investigators to be the oxybromide. Owing to the fact that it is always mixed with uranous bromide, an analysis has never been obtained.

There seemed to be, however, some basis for belief that under suitable conditions of temperature, moisture, and oxygen supply, it might be possible to obtain anhydrous uranyl bromide entirely free from the uranous compound. With this end in view, the green oxide, without any admixture of carbon, was heated in a stream of bromine, also in a current of hydrobromic acid. In each case there was apparently no action whatever other than a partial and gradual reduction to the black oxide. This slight reducing action is probably not due to the gases used, in the sense of being peculiar to them, for Zimmermann has shown that this reduction takes place whenever the green oxide is heated in a current of inactive gas such as nitrogen or carbon dioxide (*Ann. der Chem.*, ccxvi., 3; see also Richards, *Proc. Amer. Acad. Arts Sci.*, 1898, xxxiii., 423).

Both moist and dry gases were used. Mixtures of these gases and air were also tried, at different temperatures. The green oxide was then reduced by hydrogen to uranous oxide, UO₂, and this was then treated with various combinations of dry and moist bromine vapour, hydrobromic acid, and air, at various temperatures. Again the results were negative. Under these conditions the bromine did not combine to the slightest extent with the uranium. Since combination fails to take place, even in the presence of considerable quantities of oxygen, there is naturally some cause to doubt that the light coloured powder above mentioned is really an oxybromide. Possibly it is, after all, uranous bromide in a different state of aggregation.

The hydrated uranyl bromide is more easily obtained. The green oxide was reduced by hydrogen to uranous oxide, suspended in water, and heated with bromine on the steam bath. After driving off the excess of bromine, uranyl bromide remains in solution. The solution may be evaporated to the consistency of a thick syrup, and even under the best conditions the yield of crystals is very small. Moreover, it is almost impossible to wash the crystals free from the mother-liquor, since they are extremely soluble in water and alcohol, and ether decomposes the compound, setting free bromine. Hence uranyl bromide was abandoned.

Of the iodine compounds of uranium, the iodate alone seemed promising. This compound has been prepared and described by A. Ditte (*Annales de Chimie et de Phys.*, 1890, Series 6, xxi., 158), who assigns to it the anhydrous formula UO₂(IO₃)₂. The iodate was prepared by us as follows:—

To a solution of uranyl nitrate containing much nitric acid was added a solution of iodic acid, prepared by warming finely powdered iodine with nitric acid of specific gravity 1.50. Both solutions were heated to boiling before mixing. Uranyl iodate is precipitated as a yellow, finely crystalline salt, but slightly soluble in water at ordinary temperatures. At 100°, however, if some nitric acid is added, it is possible to obtain a solution containing 10 grms. of iodate to the litre. On cooling, 2.5 to 3.0 grms. of iodate crystallise out. By re-crystallising a few times, in sufficiently large vessels, it is possible to obtain a compound in a high state of purity.

The method of preparation described above is that recommended by Ditte. Although Ditte's course of procedure was carried out as exactly as possible, the compound obtained differed from that which he describes. Instead of being anhydrous, it contained one molecule of water. Inasmuch as Ditte's statement of the amount of nitric acid which he used is extremely vague, different concentrations were tried, from a solution slightly acid up to one containing 25 per cent of strong nitric acid. In every case the hydrated compound was obtained. Ditte

did not re-crystallise his compound, but our re-crystallised product was identical with that which was only once precipitated. The analysis given is the average of ten concordant analyses of material prepared from both hot and cold solutions. Both re-crystallised iodate and that precipitated only once are represented. The method of analysis is described below.

Analysis of Uranyl Iodate.

	Found.	Calculated for
	Per cent.	$\text{UO}_2(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$.
	Per cent.	Per cent.
Uranous oxide	42.54	42.34
Iodic acid	54.84	54.84
Water (by difference) ..	2.62	2.82
	100.00	100.00

In determining the composition of the iodate, a weighed quantity of the substance was used, and the percentage composition by weight calculated in the usual manner. For an atomic weight determination, however, any method which involves the original weight of a salt crystallised from solution as a factor in the calculation must, of course, be avoided on account of the ever present possibility of included mother-liquor. It was necessary, then, to determine directly the ratio of iodine to uranium, or to uranium oxide. To determine the uranium, advantage was taken of the behaviour of the iodate on ignition. When heated, the iodate is decomposed, water, oxygen, and iodine being given off, leaving uranium oxide. The process was carried on in an ordinary combustion tube of hard glass, a current of dry air being passed through the tube. Since Zimmermann has shown that the green oxide undergoes partial reduction at high temperature unless in an atmosphere of oxygen (*Annalen der Chemie u. Pharmacie*, 1886, ccxxxii., 287), a stream of oxygen was finally passed through the tube. The oxide was then cooled in an atmosphere of oxygen. Treated in this way, the decomposition of the iodate is not complete. Some iodine always remained in the oxide, even when the heat was maintained for three hours at a temperature just below the softening point of the combustion tube. To correct for this amount of iodine, the oxide was weighed, dissolved in dilute nitric acid, and the iodine precipitated as argentic iodide. The amount of iodine found in this way varied from 0.1 per cent to 1.0 per cent of the total iodine, according to the duration of the period of ignition.

Iodine was determined in another sample of material exactly similar to that used for the uranium. The method was, briefly, reduction of the iodate by sulphurous acid, and precipitation with silver nitrate. Stas has shown that silver iodate can be converted completely and without loss into silver iodide by the use of sulphurous acid, and the same method applies equally well to uranium iodate. ("Untersuchungen über die Gesetze der chemischen Proportionen über die Atomgewichte u. ihre gegenseitigen Verhältnisse," J. S. Stas, Aronstein's translation, p. 69). The iodate was suspended in 200 c.c. of water acidified with 20 c.c. sulphuric acid, cooled in ice to 0°, and pure sulphur dioxide was passed in until the solution smelled strongly of this reagent. The flask was then removed from the ice and shaken occasionally. From three to four hours is required before complete reduction takes place, and the last traces of iodate go into solution. When completely reduced, silver nitrate is added, and heated to 60° in order to cause the more coherent deposition of the precipitate.* Thus it was found possible to convert the insoluble iodate into soluble iodide without loss of iodine.

In this way the ratio of uranium oxide to iodine may be determined, regardless of the presence of occluded water in the iodate used, provided that the amount of water occluded be exactly the same in each of the samples.

* When silver iodide is precipitated in the presence of sulphurous acid, the supernatant liquid does not become clear enough to filter, even after several days, unless heated to 60°. *Vide* Stas, "Untersuchungen," p. 69.

It would obviously be more satisfactory to determine both uranium and iodine in the same sample provided a sufficiently simple method could be found.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, April 11th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

DR. R. A. LEHFELDT exhibited an Electric Heater.

The apparatus consisted of a vacuum-jacketed glass tube containing water, which was boiled by passing an electric current through a platinum spiral immersed in the liquid. Tap water is preferable to distilled water because the small electrolytic action in the former case causes the boiling to proceed quietly. Different temperatures can be obtained by using other liquids.

Mr. WATSON gave a list of liquids which he had found suitable for boiling electrically. He had used this method of obtaining a steady temperature in an apparatus for comparing thermometers.

Mr. GRANT exhibited and described an Apparatus for Vapour-pressure Measurements.

The liquid of which the vapour-pressure is required is introduced into the vacuum of a syphon barometer. This is mounted alongside an ordinary syphon barometer, and the upper extremities of both are surrounded by a bath which can be kept at any desired temperature. The levels of the mercury in the open tubes are then adjusted until the upper mercury surfaces are at the same level. The vapour-pressure is then measured by the difference of level in the open tubes. By a simple modification it is easy to investigate the vapour-pressure of a liquid in presence of air. The two chief advantages of the method are:—(1) The simplification of the temperature correction, and (2) the wide range of temperature over which it can be employed with the use of a small bath.

Prof. CALLENDAR referred to the advantages of the apparatus, and said that it appeared specially suitable for elementary laboratory measurements.

Mr. J. T. MORRIS showed an experiment illustrating the Use of Cathode Rays in Alternate Current Work.

The usual form of Braun tube was used, the rays falling upon a luminescent screen, and forming a blue spot. A solenoid conveying an alternating current was placed near the tube. The varying magnetic field caused the spot to oscillate about its mean position. To determine the maximum value of the current a switch should be arranged to rapidly replace the alternating current by a continuous one. The continuous current should then be adjusted until the maximum excursion of the spot is the same as before, and the value of the current read off from an ammeter in the circuit. For accurate work the frequency of the discharge from the induction coil exciting the tube should be adjusted until it is almost exactly in synchronism with the alternating current. The unsteadiness of the spot of light in the zero position limits the accuracy of the measurements. Mr. Morris has tried to reduce this unsteadiness by using an earthed aluminium diaphragm instead of a glass one.

Dr. HARKER thought the spot of light shown might have been made brighter by the use of a larger coil, and said the vacuum required careful attention in order to get the best results.

Mr. DUDELL pointed out that the movement of the spot about its zero position might be due to the action of the earth's magnetic field upon the varying current passing through the tube.

Mr. WILSON NOBLE suggested that the irregularity in

the position of the spot might be due to the irregular sparking of the coil, and the consequent irregular magnetic field acting upon the rays.

The CHAIRMAN said the movement was probably due to internal and electrostatic causes. He suggested the use of yttria as a luminescent material.

Mr. MORRIS, in reply, said the earth's field was too weak to account for the variable zero position. He had tried shielding the tube with an earthed copper-wire screen without any gain in steadiness.

Mr. MORRIS then showed an experiment on the Growth of Electric Currents in an Inductive Circuit.

An E.M.F. of 0.8 volt was applied to a coil wound on a ring-shaped laminated iron core. When the current had attained its steady value the E.M.F. was reversed, and the variations of the current strength shown by an ammeter. About twenty seconds were required for the current to attain its maximum value in the opposite direction. A secondary coil was also wound upon the same core, and the effect produced upon the growing current by the closing of this secondary circuit was shown. Mr. Morris has determined curves of growth for different currents, and he explained how similar curves could be used to determine experimentally the hysteresis loss in transformers.

Dr. GLAZEBROOK drew attention to the fact that this method has been applied with some slight modifications to the determination of the hysteresis loss in some 3000 H.P. transformers.

Mr. CROFT showed some Apparatus and Devices Useful in Teaching.

The method of determining graphically the focal length of a lens from the distances of conjugate foci from the centre was illustrated. The graphic solution of a quadratic equation was also shown.

An apparatus for producing and demonstrating the properties of three phase currents was exhibited and described.

Mr. CROFT then showed crystals illustrating the five regular solids, and an electric lamp with the filament in one plane useful for optical work.

The flatness of a piece of plate-glass can be tested with a scribing block. The point is adjusted to touch the glass in one position. By breathing on the glass and moving the block about it is easily seen if the point leaves the surface.

Mr. J. M. BARR said that the method could not be applied to steel. To test the flatness of a piece of steel he had made use of a small table with four legs, placed upon the surface. One leg of the table was adjustable, and was made part of a circuit containing a microphone. If the ends of the four legs are placed in one plane it is easy to test flatness by observing when the adjustable leg leaves the surface. The amount of the irregularity of the surface can be measured by having a micrometer attached to the movable leg.

The Society then adjourned until April 25th.

OBITUARY.

ALFRED CORNU.

It is with regret that we record the death of Professor Alfred Cornu, which occurred last week in Paris.

Prof. Cornu was born on March 6, 1841, and is therefore sixty-one years of age. After completing his education at the Ecole des Mines, he, in 1867, was appointed Professor of Experimental Physics at the Ecole Polytechnic, which position he still held at the time of his death. His work was almost entirely directed to optics, including diffraction, polarisation of light, and spectroscopy,

&c., though he has also published papers on acoustics, magnetism, and electrical questions.

Prof. Cornu's first paper was published in the year 1861, and his principal work, viz., on the velocity of light, was done in 1871. The amount of work he got through may be judged from the number of papers he wrote. Up to the year 1883 he wrote over seventy papers, according to the Royal Society Catalogue, besides many important ones since that date.

In 1878 Prof. Cornu was made a Member of the Academy of Sciences, and in the same year he received the Rumford Medal of the Royal Society, of which he was made a Foreign Member six years later. He was well known in English scientific circles, and has delivered three Friday Evening Discourses at the Royal Institution. The first occasion was on May 7, 1875, on "New Determinations of the Velocity of Light"; the other two lectures were delivered on May 16, 1879, and June 7, 1895; his subject on the latter occasion being "Physical Phenomena of the Upper Regions of the Atmosphere."

Prof. Cornu was a fluent and polished speaker, and a very successful manipulator and experimenter. His last lecture in England was in 1899, at the Jubilee Celebration of Sir George Stokes, his subject being "The Wave Theory of Light, and its Influence on Modern Physics."

NOTICES OF BOOKS.

Pharmacopædia; a Commentary on the British Pharmacopœia, 1898. By EDMUND WHITE, B.Sc. (Lond.), F.I.C., Pharmacist to St. Thomas's Hospital, London, and JOHN HUMPHREY. With Forty-six Full-page Plates. London: Henry Kimpton. 1901. Pp. 692.

THE word Pharmacopædia has been adopted as the title of this volume, as it exactly expresses the intention of the authors, viz., to give "information about drugs." The scope of the work is, however, restricted to the official materia medica, otherwise it would have been too unwieldy in size. In most text-books on pharmacy the subject-matter has been composed in too technical a manner; in this volume the authors have endeavoured to make the technical details of the official monographs more easy of comprehension by reference to the elementary principles laid down in those text-books, and it is believed that students will thus be enabled to secure a better grasp of the subject which pharmacists and medical practitioners are called upon to study.

The plan of the book is simplicity itself; the drugs are taken in alphabetical order beginning with "Acaciæ Gummi," or gum arabic, and going all through the list to "Zingiber," or ginger. The drug is first described, and if a chemical product, its method of production is given; this is followed by an account of its characters, and tests for its detection and recognition, and concludes with a few general notes on its properties and peculiarities.

On page 535 we come to "Notes on the Indian and Colonial Addendum (1900) to the British Pharmacopœia, 1898." Most of the drugs have been included with the object of serving—in the districts where they are produced—as equivalents of other drugs already official in the pharmacopœia; it is not, however, intended that they should be substituted for the official drugs, except where authority is expressly given in the text. Moreover, such authority is only given in those divisions of the Empire which are specially indicated in the addendum.

After the usual metrical and other tables of reference, the volume closes with the "Pharmacopædic Atlas," comprising forty-six plates giving a large number of illustrations of crude drugs and microscopical sections. The index is very full and comprises fifty-seven columns.

Methods for the Analysis of Ores, Pig-iron, and Steel, in Use at the Laboratories of Iron and Steel Works in the Region about Pittsburg, Pa. Contributed by the Chemists in charge, and Edited by F. C. PHILLIPS. Second Edition. Easton, Pa.: The Chemical Publishing Company. 1901. Pp. 170.

A KNOWLEDGE of the exact chemical composition of all raw materials and products of manufacture is becoming of more and more importance in modern iron and steel works, as in many other industries.

Not only is accuracy required, but the cry is always for greater speed in getting the results. Steel works chemists are continuously striving to shorten the time necessary for the course of the analyses, without sacrificing accuracy of results, and it may be safely said that with the great saving of time effected by recent changes in methods of analysis, greater accuracy has been secured than was possible by the older and slower methods.

The methods described in this edition are more rapid than those of the earlier edition, and are even more accurate. They comprise those in use at twenty different iron and steel works, many of which are of world-wide fame, such as the Carnegie Steel Company, the Shenango Valley Steel Company, the Pittsburg Steel Foundry Company, and many others equally well known.

In the appendix, which covers twenty-five pages, we find about a dozen methods for special determinations, such as phosphorus in coke and coal, blast-furnace cinders and their analysis, the complete analysis of chrome ore, &c.

The whole forms a volume of great value to iron and steel works chemists, who will find considerable help from the experience of others engaged in the same class of work. The book is well indexed.

Outlines of Electrochemistry. By H. C. JONES. New York: The Electrical Review Publishing Co. 1901.

THIS little book consists of papers on the most important chapters of electrochemistry, reprinted from the *Electrical Review*. Starting from the basis of the relations between osmotic pressure and gas pressure, the chief facts and theories of electrochemistry are put forward in simple graphic language, specially likely to be appreciated by those whose scientific knowledge is not extensive. This is not to say, however, that the papers are in any degree "popular." The author has successfully kept before him the requirements both of the student of chemistry and the electrical engineer, and shows himself particularly able in his grasp of the difficulties likely to occur to those who are reading the subject for the first time, forestalling such difficulties by short accurate explanations; and he is an adept also in stating the gist of a question in a few concise words, so that, while a wide range of the subject is covered in short space, the book by no means presents the aspect of a mere dry enumeration of facts, but is really interesting reading.

A Travers la Matière et l'Energie. By Docteur F. E. BLAISE. Paris: Librairie Ch. Delagrave.

FROM the preface to this astonishing book we conclude that it represents an attempt to apply the scientific argument as the basis of philosophical research, and the result appears to lead us to the conclusion that Epicurus and the alchemists were after all in the right, and that our wanderings from the paths marked out by them have only led us to hopeless error. We have before us the old hypothesis that the atoms of every element have resulted from the coalescence of particles of "primether," which is at once the basis common to both matter and energy; these particles in their coalescence obey the laws of electricity and mechanics. All properties of matter are proved to be reducible to movement.

After a good deal of discussion of the laws of electricity and of induction, we pass to the application of the laws of

mechanics, &c., to moral and social problems, to a parallel between religious dogma and notions of energy and matter, and, incidentally, to a refutation of Darwinism, which was foretold in an earlier part of the work in the sentence:—"C'est l'appareil qui crée la fonction." It would be an easy, if profitless, task to point out many similar instances of unguarded or erroneous assertions; we cannot refrain, however, from calling attention to the paragraph on page 320, which embodies the author's ideas as to the descents of mules and hybrids.

We are told that the doctrine of the progressive variation of individuals derived from a common type has still, and will always have, its adherents, whose enthusiasm is the result of some species of moral blindness and obliquity. This is perhaps the mildest description applied to those who presume to differ from M. Blaise. Those who are sufficiently curious to glance through the book to extract some passing amusement from its mixture of doubtful philosophy and still more doubtful science will probably feel that at any rate they err in good company when they do not agree with much that M. Blaise tell us.

Introduction à l'Etude des Métaux. By ALFRED DITTE. Paris: Société d'Éditions Scientifiques. 1902.

THE subject of the metallic elements is attacked in this book in a somewhat original way, likely to lead to wider and more comprehensive views than the more usual method, without, however, sacrificing a detailed knowledge. Instead of studying each metal and its compounds separately, the student first reads chapters on the geological occurrence of the metals, their origin, and extraction from their ores. Hence he passes to their general physical properties, and the causes which modify these properties. The metals are then considered in their relations to other bodies; firstly, the other elements, then acids, bases, and salts. A similar method of treatment undoubtedly simplifies the study of the carbon compounds, where a general knowledge is to be desired rather than any special attention to details, and no doubt this method will commend itself to students and teachers of inorganic chemistry. The book is strictly methodical and precise, especially as regards the general review of the subject of the action of the metals, the explanations by reference to thermochemical phenomena being excellent. The section on the persistence or disappearance of the properties of an element in various compounds would probably fail to give the student very definite views, but at any rate he would have the minimum amount to unlearn on proceeding to more exhaustive treatises or original publications.

Manuale del Chimico e dell' Industriale. By DOTTOR LUIGI GABBA. Milan: Ulrico Hoepli. 1902.

THE reception of this handbook of chemistry and allied industries has warranted the production of a third revised and enlarged edition, in which special attention is paid to analytical processes. The analytical tables of Will are included, in the hope of making the book useful to students; these are printed on twelve separate sheets, and ingeniously fastened within the cover of the book, so as to be readily detached, a great convenience for use in the laboratory. The first three chapters consist chiefly of tables of physical and chemical data, including copious lists of the densities and concentrations of salts and organic substances, and tables of solubility of various bodies in water and other solvents. Unfortunately this part of the book is by no means free from inaccuracies and misprints; we notice, for instance, that though the table of atomic weights from Lunge's "Taschenbuch" includes praseodymium and neodymium, in other places in the book didymium is still to be found amongst the elements, and other errors might be cited. The fourth chapter contains short descriptions of analytical processes relating to water, glass, oils and fats, manures, &c., and also assaying processes. This more descriptive portion con-

tains a really wonderful amount of information in a short space, and it would be unreasonable to expect fuller accounts of the various processes within the limits of the book. Much useful matter is to be found in the manual, which deserves to be largely employed as a book of reference by analytical and technical chemists and students of chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 12, March 24, 1902.

Direct Hydrogenation of Oxides of Carbon in presence of certain Finely Divided Metals.—Paul Sabatier and J. B. Senderens.—Cobalt when reduced from its oxide by means of hydrogen below 450°, behaves in exactly the same manner as reduced nickel both with regard to carbonic oxide and carbonic anhydride, these being regularly hydrogenated and transformed into methane. These changes do not start until a high temperature is attained. The reaction, beginning at about 300°, becomes more rapid at 360°, and still more rapid at 400°. The reaction takes place according to the equation $\text{CO}_2 + \text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$. Finely divided platinum effects the direct hydrogenation of carbon dioxide or carbon monoxide. When the action takes place below 420°, there is no appreciable formation of methane. The same occurs with palladium and also with iron reduced from its oxide by prolonged action of hydrogen at 500° C. Finely divided copper has no such action.

Boiling-point of Selenium and some other Pyrometric Constants.—Daniel Berthelot.—The author determines with great accuracy the boiling-point of selenium and other pyrometric constants. His results are expressed in the following table:—

Boiling-point of selenium ..	690° + $\frac{\text{H} - 760 \text{ m.m.}}{10 \text{ m.m.}}$
Boiling-point of cadmium ..	778° + $\frac{\text{H} - 760 \text{ m.m.}}{9 \text{ m.m.}}$
Boiling-point of zinc	918° + $\frac{\text{H} - 760 \text{ m.m.}}{8 \text{ m.m.}}$
Melting-point of silver	962°
Melting-point of gold	1064°

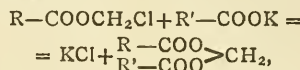
Thermic Equivalent of Dissociation, of Vapourisation, and Heat of Solidification of Ammonia.—M. de Forcrand.—The author determines the heat of solidification of a gaseous molecule from a knowledge of the dissociation and the heat of formation of a certain number of its dissociable compounds. Such a method is of great use when direct measurement is impossible or difficult, as is usually the case with gases.

An Acid Monosodic Orthophosphate.—H. Giran.—The author examines the crystals which are recovered from the cylinder in which commercial metaphosphoric acid is prepared. He estimates directly the phosphoric acid, soda, and water, and thus deduces the formula $\text{P}_2\text{O}_5 \cdot \text{NaH}_2$. This is the monosodic salt corresponding to M. Joulie's sesquisodic phosphate.

Sesquisodic Phosphate.—J. B. Senderens.—The author further discusses M. Joulie's paper on the new phosphate of soda.

Some New Compounds of Methylene.—Marcel Descudé.—The author has already shown that zinc chloride provokes the very rapid action of trioxymethylene with an acid chloride, $\text{R} \cdot \text{COCl}$, giving rise to the compound $\text{R} \cdot \text{COO} \cdot \text{CH}_2\text{Cl}$. Besides this, during the distillation of the crude product in vacuo, the product

$(\text{R} \cdot \text{COO})_2\text{CH}_2$ is present in varying proportions, but always in considerable quantity. By repeating this reaction on a great number of the acid chlorides the author now establishes the fact that such a reaction is absolutely general. However, in the case of the bibasic acid chlorides (those of succinyl and phthalyl), when the action is very energetic, the distillation, even in vacuo, provokes complete decomposition, and, as a residue, the theoretical quantity of the corresponding anhydride is found proportionate to the weight of acid chloride employed. Finally he obtains a series of mixed compounds in accordance with the reaction—



which regularly occurs when the mixture is heated for at least three hours to a temperature varying with the radicle but always above 160°.

No. 13, March 31, 1902.

This number contains no chemical matter.

MISCELLANEOUS.

A New Oxide of Molybdenum, the Semipentoxide of Molybdenum.—P. Klason.—This paper deals with the examination of the various compounds in which molybdenum is pentatomic, compounds already partly announced by Berzelius and De Bray. The author proposes the name *molybdenyl* for the trivalent radical MoO , and *molybdone* for the divalent radical MoO_2 . *Chloride of Ammonium and Molybdenyl*, $\text{MoOCl}_3 \cdot 2\text{NH}_4\text{Cl}$.—Two hundred grms. of molybdate of ammonium are dissolved in 600 c.c. of fuming hydrochloric acid, and for each atom of molybdenum present we add 1 molecule of iodide of ammonium (or concentrated HI) and 0.1 (or 1) molecule of chloride of ammonium; this is distilled on the sand-bath, iodine is given off, and when the fumes of this latter have almost ceased to appear, the cooled residue is saturated with hydrochloric acid gas, the contents become dirty brown or green in colour. After a few hours, beautiful grass-green octahedric crystals are deposited which are drained after washing with concentrated hydrochloric acid. This body is soluble in water, with a yellowish-brown colour, but with partial hydrolysis. The solution has become partially oxidisable in the air with the formation of the molybdenum blue; the addition of hydrochloric acid brings back the green colour. Alcohol acts like water, and separates out chloride of ammonium. *Hydrate of Molybdenyl*, $\text{MoO}(\text{OH})_3$.—The solution of the preceding salt treated with an excess of ammonia gives a precipitate, and the liquid contains a good deal of MoO_3 (De Bray). But if the operation is carried out in the cold, in dilute solution, and by gradually adding, while stirring, the strictly necessary quantity of ammonia, the molybdenum is deposited integrally in the form of a precipitate resembling ferric hydrate, but slightly lighter in colour; this is hydrate of molybdenyl, and is rather difficult to collect and drain on the filter; it is insoluble, or only slightly soluble, in alkaline solutions, but an excess of these latter alters the product, giving soluble molybdates. It has no acid properties. *Semipentoxide of Molybdenum*, Mo_2O_5 .—The preceding hydrate, carefully dried in a current of carbonic acid, gives the corresponding oxide, a black-violet powder difficultly soluble in hydrochloric or sulphuric acids. *Chloride of Molybdenyl*, MoOCl_3 .—M. M. Blomstrand (*Journ. f. Prakt. Ch.*, vol. lxxi., p. 466) and Putzbach (*Lieb. Ann.*, vol. cci., p. 123) obtained, by the action of the chloride on a mixture of MoO_2 and carbon, an oxychloride which should be MoOCl_4 . The author thinks that this product consists principally of MoOCl_3 , as, when re-dissolved in concentrated hydrochloric acid and treated with sal-ammoniac, it gives directly the double salt described at the commencement of this paper.—*Berichte*, vol. xxxiv., p. 148.

MEETINGS FOR THE WEEK.

- MONDAY, 21st.—Society of Arts, 8. (Cantor Lectures). "Glass for Optical Instruments," by Richard T. Glazebrook, M.A., D.Sc., F.R.S.
- TUESDAY, 22nd.—Royal Institution, 3. "Recent Methods and Results in Biological Inquiry," by Allen Macfadyen, M.D., B.Sc., Fullerian Professor of Physiology, R.I.
- WEDNESDAY, 23rd.—Society of Arts, 8. "Opto-technics," by Prof. Silvanus P. Thompson, D.Sc., F.R.S.
- THURSDAY, 24th.—Royal Institution, 3. "The Oxygen Group of Elements," by Prof. Dewar, M.A., LL.D., D.Sc., F.R.S., Fullerian Professor of Chemistry, R.I.
- FRIDAY, 25th.—Royal Institution, 9. "X Rays and Localisation," by James Mackenzie Davidson, M.B., C.M.
- Physical, 5. An Exhibition of a Mechanical Break for Induction Coils, by Dr. Dowson Turner. "A Temperature Indicator for Use with Platinum Thermometers, in which Readings are Automatically Reduced to the Gas Scale," by R. S. Whipple. "Note on the Compound Pendulum," by S. A. F. White.
- SATURDAY, 26th.—Royal Institution, 3. "British National Song" (with Musical Illustrations), by William H. Cummings, Mus.D. (Dub.), F.S.A., Hon. R.A.M., Principal of the Guildhall School of Music.

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THE CHEMICAL NEWS.

VOL. LXXXV., No. 2213.

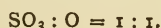
PERSULPHURIC ACID.*

By HENRY E. ARMSTRONG, V.P.R.S.,
and
T. MARTIN LOWRY, D.Sc.

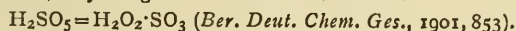
ALTHOUGH it was observed by Faraday in 1834 that "if the acid were very strong, a remarkable disappearance of oxygen took place" on electrolysing aqueous solutions of sulphuric acid ("Researches in Electricity," Series vii., § 728), it was not until 1878 that its disappearance was at all satisfactorily accounted for by the discovery of *persulphuric acid* by Berthelot.

Only the anhydride, S_2O_7 , was isolated by Berthelot, but he concluded that the corresponding acid was formed (1) on dissolving the anhydride in water, (2) on electrolysing strong solutions of sulphuric acid, and (3) by the interaction of hydrogen peroxide and ordinary sulphuric acid. The correctness of these conclusions appears to have been regarded as beyond question after Marshall had discovered in 1891 that well-defined salts of "Berthelot's acid" could be prepared by electrolysing solutions of potassium- or ammonium-hydrogen sulphate. Doubt arose, however, when Caro, in 1898, discovered that if Marshall's salts were acted on by sulphuric acid, a new acid was obtained having properties markedly different from those associated with Berthelot's acid. "Caro's acid" soon acquired importance as an oxidising agent, owing to the good use that was made of it by Bamberger and by von Baeyer and Villiger.

Having found that Caro's acid liberated iodine very rapidly, whereas Berthelot's acid acted but slowly on iodides, these latter chemists were able to devise a process by which the one acid could be estimated in presence of the other. By removing sulphuric acid by means of barium phosphate, they obtained a solution containing Caro's acid and Berthelot's acid, in which they determined the amount of each of these substances as well as the amount of sulphate to which the persulphuric acids gave rise when decomposed. Their results led them to conclude that the ratio of sulphur to active oxygen in Caro's acid was—



Placing the simplest possible interpretation upon this result, they assigned to the acid the formula—

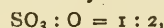


Meanwhile the problem had been studied from a somewhat different point of view by Lowry and West (*Chem. Soc. Trans.*, 1900, 950), who had determined the equilibrium subsisting between hydrogen peroxide and "persulphuric acid" in presence of sulphuric acid and water, and had found that the ratio which the hydrogen peroxide bore to total "persulphuric acid" was entirely dependent on the ratio which the water bore to the sulphuric acid—the ratio of hydrogen peroxide to "persulphuric acid" being ultimately the same in a mixture prepared from hydrogen peroxide and sulphuric acid as in a solution of equal strength prepared by electrolysis. The experimental curve approximated very closely to a curve deduced from an equation of the fourth order, and assuming that the chief product of interaction was a persulphuric acid of the series $H_2O_2 \cdot nSO_3$, it was to be supposed that it was the fourth term of the series, viz., $H_2O_2 \cdot 4SO_3$. But there were indications that some simpler acid was also present in small quantity.

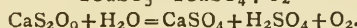
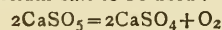
These results applied mainly to concentrated solutions, 85 per cent of the change taking place between the limits expressed by the formula $H_2SO_4 \cdot H_2O$ and $H_2SO_4 \cdot 4H_2O$; and virtually no peroxidation of the sulphuric acid took place below the limit expressed by the formula $H_2SO_4 \cdot 6H_2O$. Von Baeyer and Villiger, on the other hand, had dealt with a product existing in dilute solution. The different conclusions deduced from the two sets of results were, therefore, not necessarily discordant; it was possible that the product examined by Baeyer and Villiger had been formed by hydrolysis from the "higher" acid which Lowry and West's observations had indicated was present in concentrated solutions. It is also to be noted that the determination of the ratio of active oxygen to sulphur is sufficient to determine the composition of the acid only in the case of the acid being one of the $H_2O_2 \cdot nSO_3$ series; obviously, other types of "persulphuric acid" are possible.

If we consider what must be the properties of the persulphuric acids generally, it is clear that whereas the salt of a dibasic acid of the formula H_2SO_5 would remain neutral on withdrawal of the peroxide oxygen, salts of higher acids would yield more or less sulphuric acid when decomposed. As a carefully neutralised solution of Caro's acid becomes acid when heated, the salt originally present in it cannot be one derived directly from the acid H_2SO_5 —assuming that this is dibasic.

We are much indebted to Mr. A. J. Cook for having made a long series of determinations which show that the ratio of the increase in acidity to active oxygen lost is—



a result which finds expression in the formula $H_2S_2O_9$, but is in direct opposition to the formula H_2SO_5 ; thus, supposing the calcium salt to be used:—



The probability that the acids in question have the composition suggested is considerable, if the manner in which sulphuric acid may be expected to undergo electrolysis be taken into account. Strong solutions of the acid may be supposed to contain both sulphuric and disulphuric acids, and it may be expected that both would "peroxidise"; on electrolysis, the former would give perdisulphuric acid, and the latter pertertra-sulphuric acid, thus—

$HO \cdot SO_2 \cdot OH$	$HO \cdot SO_2 \cdot O$
Sulphuric acid.	Perdisulphuric acid.
$HO \cdot SO_2 \cdot O \cdot SO_2 \cdot OH$	$HO \cdot SO_2 \cdot O \cdot SO_2 \cdot O$
Disulphuric acid.	Pertetrasulphuric acid.

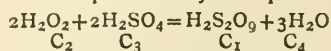
An acid of the formula $H_2S_2O_9$ may be regarded as the anhydro-acid derived from permonosulphuric acid, i.e., as $HO \cdot O \cdot SO_2 \cdot O$. It is scarcely necessary to say that the interpretation now put upon the data afforded by solutions of Caro's acid will need to be verified, and cannot be accepted as final until salts of the acid have been isolated. This we are engaged in doing.

Further consideration, in the light of the facts brought forward by Baeyer and Villiger and in the present communication, of the results arrived at by Lowry and West, has served only to confirm the conclusion that the chief product of oxidation of sulphuric acid by hydrogen peroxide in presence of less than 50 per cent of water is an acid richer in sulphur trioxide than perdisulphuric acid, and to justify the assumption on which they based the formula $H_2S_4O_{14}$ —namely, that the acid is a member of the series $H_2O_2 \cdot nSO_3$. Lowry and West determined only the ratio of peroxide oxygen to persulphuric oxygen, and paid no attention to the total oxidising power of the solution. That they were justified in this course is apparent from the fact that no change in the ratio of the two forms of oxygen was observed on varying the strength of the

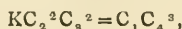
* A Paper read before the Royal Society, March 20, 1902.

peroxide solution from 10 to 40 "volumes," nor was any change observed as the oxidising power gradually decreased when the acid decomposed.

If the main product of the interaction had been an acid of the formula $\text{H}_2\text{S}_2\text{O}_9$, this would not have been the case, as the equilibrium represented by the equation—



would depend on the total oxidising power of the solution as well as on the proportion of sulphuric acid and water; this is seen most clearly when the equation of mass action,—



is transposed into the form—

$$\frac{\text{C}_1}{\text{C}_2} = \text{K} \left(\frac{\text{C}_3}{\text{C}_4} \right)^2 \cdot \frac{\text{C}_2}{\text{C}_4},$$

which indicates that the ratio C_1/C_2 of persulphuric oxygen to peroxide oxygen depends not only on the ratio C_3/C_4 of sulphuric acid to water and on the concentration C_4 of the water in the solution, but also on the actual concentration C_2 of the hydrogen peroxide. The fact that the equilibrium is independent of total oxidising power can only be explained if the chief products of interaction are members of the series $\text{H}_2\text{O}_2 \cdot n\text{SO}_3$, or hydrates thereof.

As there was no sufficient evidence to justify the assumption that a third persulphuric acid was present in the solutions they examined, Lowry and West had no alternative but to regard Caro's acid as pertetrasulphuric acid, and their simpler member of the series as the acid corresponding to Marshall's salts. The determination of the ratio of sulphur to active oxygen by Baeyer and Villiger has rendered such a limitation impracticable, and we now feel not only that it is justifiable, but that we are compelled to postulate the existence of *at least three persulphuric acids, viz.,—*

Pertetrasulphuric acid $\text{SO}_3 : \text{O} = 4 : 1$
 Perdisulphuric acid $\text{SO}_3 : \text{O} = 2 : 1$
 Peranhydrosulphuric acid (Caro's acid). $\text{SO}_3 : \text{O} = 1 : 1$

In carrying out his experiments, Mr. Cook nearly neutralised solutions of Caro's acid by means of a carbonate, and then neutralised the liquid by means of either sulphuric acid or caustic soda, portions being taken out and tested with methyl-orange. Measured portions of the neutral solution were run as quickly as possible into flasks containing a little dilute sulphuric acid to arrest decomposition; the persulphuric acids were then estimated by Baeyer and Villiger's method. Portions of the same solution were heated at 100° until all oxidising power was lost, and the acidity developed was estimated by caustic soda, using methyl-orange as indicator.

Solution I.—This was prepared by digesting potassium persulphate at $60-70^\circ$ with a solution containing only 10 per cent of sulphuric acid. At the end of about two hours the cooled solution was diluted and neutralised with chalk. The amount of iodine liberated at once by the Caro's acid present, expressed in terms of decinormal thiosulphate solution, was equivalent to 41.54 c.c.; the amount of iodine liberated slowly by the perdisulphuric acid present was equivalent to 1.05 c.c. The acid liberated on warming the solution was equivalent to 22.06 c.c. The calculated amount, assuming the ratio $2\text{O} : \text{SO}_3$, would be $1.05 + 41.54 = 21.80$ c.c.

In the subsequent experiments 15 grms. of potassium persulphate was digested with from 35 to 25 c.c. of concentrated sulphuric acid at the ordinary temperature during one to two hours. The solution was then diluted with ice and neutralised: in Experiments 2, 3, 4, and 6 with chalk, in 5 with sodium bicarbonate, and in 7 with sodium carbonate, using phenolphthalein as indicator. In Experiment 7 the solution was mixed with excess of caustic soda before warming it to decompose the per-salts, and the excess was subsequently determined. No hydrogen peroxide

was present except in solution 5, in which case the amount was determined by permanganate and allowed for.

The following are the results obtained in terms of decinormal solutions:—

		Caro's acid.	Perdisulphuric acid.	Acid liberated.	
				Found.	Calculated.
I.		41.54	1.05	22.1	21.8
II.		38.8	5.91	26.6	25.3
III.		35.0	2.77	20.2	20.3
IV.		39.24	2.24	21.3	21.8
V.		37.3	1.56	21.5	20.2
VI.		49.8	3.43	28.7	28.3
VII.		23.3	0.71	12.2	12.4

ON THE HEATLESS CONDITION OF MATTER:

BEING AN EXTENSION OF THE KINETIC THEORY.

By JAMES HANCOCK BRINKWORTH

and
GEOFFREY MARTIN, B.Sc.(Lond.).

ACCORDING to the kinetic theory, all bodies are composed of molecules in a state of very rapid motion. In a solid the molecules are not in absolute contact, but vibrate rapidly about fixed centres.

Consider a solid placed in an infinitely strong and unyielding cylinder, made out of a good heat-conducting substance, and let the whole be kept in a liquid bath at a constant temperature.

The solid is now slowly compressed. As the compression proceeds and the molecules are driven closer together, heat will be evolved; but the surrounding liquid will conduct this away, and if the compression be slow enough, the temperature of the whole system will remain constant. But this compression cannot continue beyond a certain amount, for ultimately the molecules will be driven into absolute contact, and will be so tightly pressed, the one against the other, as to be absolutely unable to move relatively to each other.

Therefore, in this condition the molecules can possess no kinetic energy or relative motion of any description.

Now, according to the kinetic theory, the temperature of a body is measured by the kinetic energy of its molecules.

So that our solid, when in the above state, has been by pressure reduced to the absolute zero of temperature. Here, then, we are dealing with a very remarkable case.

We have here a solid at the absolute zero of temperature, in the midst of a medium at a much higher temperature, and yet the solid (on account of the enormous pressure to which it is subjected) is unable to take up the surrounding temperature, but persists in its heatless state.

But if the pressure be suddenly released, then the solid immediately regains the power of acquiring heat from neighbouring bodies at higher temperatures, and its temperature will rapidly rise from absolute zero, until it reaches that of the surrounding material—following in this the law of thermal equilibrium.

It therefore appears to be a necessary consequence of the molecular theory that at a *very great pressure* matter must be reduced to a peculiar condition in which it will not obey the law of thermal equilibrium; and this law states that:—*If a body A be in intimate contact with a body B, and both be at different temperatures, then the bodies are in a state of unstable thermal equilibrium, and the temperature of the one will rise and the other fall until a common temperature be obtained.*

Now the pressure at which this remarkable physical condition becomes manifest depends upon the nature of the material, and will alter with the temperature. As the temperature falls, and the kinetic energy of the molecules becomes less, a smaller pressure will suffice to bring the molecules into contact. So that, in general, to each tem-

perature there must correspond a minimum pressure which just suffices to bring matter into this new condition, and a curve could be traced, did we possess the experimental data, showing the variation of this minimum pressure with the temperature, in much the same way that boiling-point and freezing-point curves can be traced.

At ordinary temperature, of course, the pressures will be terrific—probably beyond our experimental power—but at very low temperatures the case is different, and a moderate pressure will suffice to bring about this new condition. But the "pressure" here is made up of two parts—the external and the internal, the latter being due to mutual molecular attraction.

So that even if the external pressure is zero, yet the molecules will be under a very considerable internal pressure. And the very interesting conclusion must be drawn that to this internal pressure alone there must correspond a definite temperature above absolute zero, at which this new condition is induced in matter.

So that if we cool down a body under zero external pressure to the low temperature corresponding to the internal pressure, at this point its temperature will abruptly drop to the absolute zero.

The usual assumption, therefore, that all substances can be cooled continuously and uniformly down to the absolute zero is incorrect.

Each substance can only be cooled continuously and uniformly down to a minimum temperature, depending upon the total pressure, and any further cooling below this causes its temperature to drop more or less abruptly and of its own accord to the absolute zero, no matter whether the surrounding temperature be above absolute zero or not.

The heat energy which thus disappears going to increase intramolecular motion. In fact, in order to maintain a "temperature state" in matter there is required a certain minimum amount of energy, in exactly the same way that a certain minimum amount of energy is required in order to maintain matter in the "liquid" and "gaseous" state.

This minimum amount of molecular energy (contained in unit mass)—which, of course, depends upon the pressure and upon the nature of the material—we will call the "starting energy." The "starting energy," therefore, is exactly analogous to the "heat of fusion" and "heat of volatilisation"; also, for brevity, we will call that temperature at which matter enters this new physical condition the "heat-point," and this in its turn is exactly analogous to the "melting-point" and "boiling-point"—marking as it does the temperature at which matter enters a new physical condition. Other conditions being equal, the value of the heat-point will increase with the molecular weight, just as the melting-points and boiling-points do. With hydrogen, for example, it occurs at very low temperatures; but, in the case of the heavy metals, it occurs at a temperature considerably above absolute zero.

To illustrate the theory, we will take the case of a body at normal temperatures and under a very great pressure, but a pressure not sufficiently great to bring the molecules into contact.

Let the body be cooled progressively, keeping meanwhile the pressure constant.

Then ultimately a temperature will be reached, whereat the pressure overcomes the kinetic energy of the molecules and jams them tightly together.

At this point the temperature of the compressed body will fall of its own accord to the absolute zero of temperature, no matter whether the temperature of the surrounding material be above absolute zero or not. Further, if its molecules are all of the same average weight, this change of temperature will take place more or less suddenly; i.e., the temperature of the solid will, when a certain temperature be passed, drop more or less abruptly to absolute zero.

The probability of this becomes manifest when we consider the nature of the change. For as compression proceeds at a constant temperature, and as the molecules

become crowded more and more closely together, their kinetic energy (the total amount of which must remain constant, since the temperature remains constant), partakes less and less of a translatory, and more and more of a rotational character.

For in a crowded condition any translatory movement on the part of a molecule will immediately bring it into collision with neighbouring molecules, as there is but little play space between them; and the inevitable result of a succession of such collisions will be to gradually convert all the translatory energy of the molecules into rotational energy, provided only we wait long enough.

At the moment before actual molecular contact takes place, we may conceive that all translatory energy has given place to rotational energy.

So that we may liken the molecules at this instant to a vast number of rapidly whirling spinning-tops, almost devoid of translatory movement. The moment these are crowded together, so as to brush against each other as they rotate, enormous frictional forces, due to the molecules grinding one against the other, will start into being and rapidly reduce all to a state of quiescence.

These frictional forces will be all the more marked from the fact that molecules are not smooth round balls, but rather are complicated congeries of atoms, which in their turn have an angular geometrical shape—a statement the truth of which is proved by the science of "stereo-chemistry."

The internal intra-molecular disturbances brought about by the grinding together of the molecular systems will be very great at these low temperatures, and perhaps explains the great display of light and electricity which Dewar has shown to take place when bodies are cooled to a very low temperature, such manifestations being the result not of molecular but of intra-molecular disturbances.

From the above it is obvious that a body cannot acquire for any length of time every temperature; there is in all cases a superior and inferior limit. We may express this by saying that the temperature scale of a body is not a continuous function, but vanishes abruptly at two points—(a) the temperature at which the body decomposes, (b) at the heat-point. Only for values of temperature intermediate between a and b is the temperature scale continuous.

University of Berlin, March 26, 1902.

NOTE ON FREE ACID IN SUPERPHOSPHATE.

By J. OSTERSETZER, F.I.C., F.C.S.

SUPERPHOSPHATES, especially those newly manufactured, when being titrated with N/2 or N/10 NaHO solutions in order to determine the free acid present, show beyond the point of opalescence a certain formation of CaHPO_4 precipitate, which can be distinctly noticed before the neutral reaction takes place with litmus or paranitrophenol; by using such indicators as dimethylamidoazobenzol, methyl-orange, or alizarin-sulphonic acid, intermediate tints will appear between the point of opalescence and that of neutrality. As regards phosphoric acid, H_3PO_4 , Berthelot first observed that on the substitution of the first hydrogen this acid acts as a powerful acid; on the substitution of the second hydrogen as a weaker acid like an organic acid; and on the substitution of the third hydrogen as an alcohol. These different degrees of acidity can be shown by the use of methyl-orange, phenolphthalein, and blue, C_4B , corresponding respectively with the formation of monobasic, dibasic, and tribasic phosphate. It appears, however, that as far as the combination of orthophosphoric acid and lime is concerned, the former may, under given conditions, become to a certain extent loosely attached to $\text{CaH}_2\text{P}_2\text{O}_7$, pointing to a possible state of polymerisation of H_3PO_4 . It may be interesting to note that by the action of H_3PO_4 upon the rhombic tablets of the tetra-

hydrocalcic phosphate, $\text{CaH}_4\text{2PO}_4$, at the normal temperature, and the ratio of 6 mols. $\text{CaH}_4\text{2PO}_4$ to 1 doubled mol. H_3PO_4 , a substance can be obtained having all the appearance of one chemically combined; the same occurring at 100°C . when 3 mols. $\text{CaH}_4\text{2PO}_4$ in solution to 1 doubled mol. H_3PO_4 is used.

Staudenmaier (1893) made similar observations by obtaining a compound, $\text{KH}_2\text{2PO}_4$, corresponding to the doubled molecule of H_3PO_4 by the action of KH_2PO_4 upon H_3PO_4 . On the other hand, H. Joulie (1902) shows that there exists a compound, $\text{Na}_3\text{H}_2\text{2PO}_4$, intermediate between monosodic and disodic phosphates, the addition of phosphoric acid to Na_2HPO_4 being less than would otherwise be requisite for $\text{NaH}_2\text{2PO}_4$ (*Comptes Rendus*, vol. cxxiv., No. 10, March 10, 1902).

When the normal salt $\text{Ca}_3\text{2PO}_4$ is treated with H_3PO_4 with the object of forming $\text{CaH}_4\text{2PO}_4$, it may thus be imagined that in the first instance such an apparent excess of phosphoric acid as pointed out above must be used as to counteract the dissociating power of water at 100°C . upon the constitution of tetra-hydrocalcic phosphate; after cooling and on dissolving in water at the ordinary temperature for analytical purposes, a portion of that phosphoric acid will appear as excessive free acid, leaving a residue of the same still loosely combined; the former it is proposed to determine by an intermediate tint of alazarin-sulphonic acid; the change from bright to slightly dark yellow when titrated with NaHO solution coinciding closely with the point of opalescence.

Julius Wagner, in common with Bredig and Winkelbach, attributes the appearance of intermediate tints in the presence of phosphates or other substances to ionisation of the indicators.

The Laboratory,
Messrs. W. and H. M. Goulding, Lim.,
North Wall, Dublin, April 14, 1902.

THE NEW GAS FROM RADIUM.

By E. RUTHERFORD, M.A., D.Sc.,
Macdonald Professor of Physics, McGill University, Montreal,
and
Miss H. T. BROOKS, M.A.

IN a recent number of the *Comptes Rendus*, an account was given by Curie of the evidence of the existence of a new gas from radium, which possesses remarkable physical properties. A specimen of very radio-active radium was placed in a glass vessel connected with a mercury pump. On exhausting to a low vacuum and allowing the apparatus to stand, the pressure steadily increased. When the very small volume of gas thus collected flowed along the glass tubes, it rendered them phosphorescent, and if left in for some time, rapidly blackened them. The gas itself was powerfully radio-active, *i.e.*, it continuously gave out a type of Röntgen rays which made gases partial conductors of electricity, and rapidly acted on a photographic plate. This gas preserves its radio-active power for several weeks.

For some time past, one of the authors had been independently investigating one of the most remarkable properties of radio-active substances, namely, the power of continuously emitting radio-active particles of some kind. The term "emanation" was applied to the substance thus emitted, as there was no evidence at the time whether the material emission was a vapour of the substance, a radio-active gas, or particles of matter each containing a large number of molecules.

The "emanation" from thorium compounds was shown to retain its radio-activity for several minutes, and possessed the remarkable property of causing every substance in the neighbourhood of the thorium to become itself radio-active for several days. The specimens of impure radium then in the possession of the author did not possess the power of emitting such an emanation; but

Dorn, using a later and more active preparation of radium, showed that it possessed the same emanating power as thorium. One of the most interesting properties of excited radio-activity is that it can be concentrated in an electric field on the cathode, so that a very fine wire of any metal can be made to act like a powerfully radio-active substance for several days.

A short time ago one of the authors published an account of the effect of temperature on the emanating power of radio-active substances, in the *Physikalische Zeitschrift*. In the paper it was shown that the emanating power of thorium increased with rise of temperature to about a red heat, but on heating to a white heat the emanating power was destroyed, and could not be recovered. An examination of a specimen of radium obtained from De Haen, Hanover, showed that the effect of temperature on its emanating power was very large. When the substance was heated below a red heat, its emanating power increased over 10,000 times, but was to a large extent destroyed by heating to a higher temperature. The emanation, obtained by passing a slow current of air over heated radium, was found to preserve its radio-active powers for weeks, when kept in a closed metal vessel. The radio-activity slowly decayed, but was still quite appreciable after a month's interval.

The question now arose, if any physical experiments could be devised to settle the problem as to whether the emanation was in reality a radio-active gas, driven off from the substance, or a vapour of the substance, or a material emission of particles much larger than molecules. Experiments on thorium showed that no appreciable volume of gas could be collected by leaving thorium oxide in a vacuum tube connected with a mercury pump. No new lines were observed in the spectrum of the gas. The amount of the emanation thus given off was thus too small to detect by its volume in this way, but the electrical conductivity produced by the emanation in the gas with which it is mixed is often very large, and can be used as a measure of the amount of emanation present. The emanation gives out a type of radiation which ionises the surrounding gas. When a strong electric field is applied, the current through the gas reaches a maximum value, and is then a measure of the total number of ions produced per second, multiplied by the charge on the ion.

By determining the rate of diffusion of the emanation into air or other gases, using the electrical method, it is possible to obtain an approximate estimate of its molecular weight. The coefficient of inter-diffusion of most of the simple gases have long been known, and the results show the coefficient of diffusion of one gas into another is inversely proportional to the square root of the product of the molecular weights. If therefore the coefficients of diffusion of the emanation into air is found to have a value lying between that of two gases, A and B, we can conclude that the molecular weight of the emanation lies between the molecular weights of A and B.

The apparatus employed was similar to that used by Loschmidt (*Wiener Akad.*, 1871) in his experiments on the coefficient of interdiffusion of gases in the year 1871.

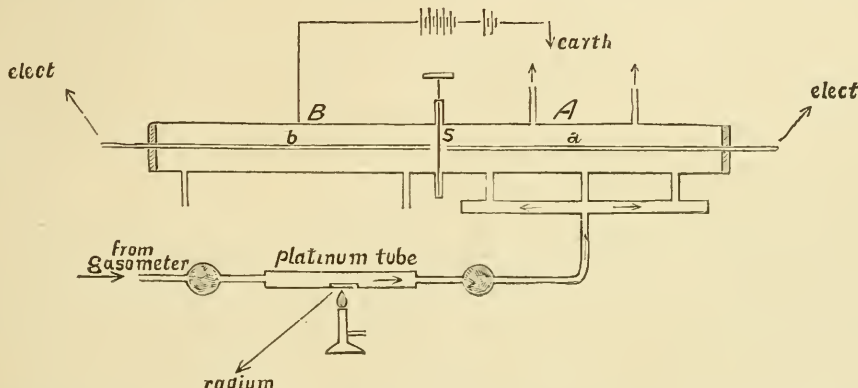
Fig. 1 shows the general arrangement. A long brass cylinder, A, B, 6 c.m. in diameter, 73 c.m. long, was divided into two equal parts by a movable metal slide, S. The ends of the cylinder were closed with ebonite stoppers. Two insulated brass rods, *a* and *b*, each half the length of the tube, passed through the ebonite stoppers, and were supported centrally in the tube. The cylinder was insulated and connected to one pole of a battery of 300 volts, the other pole of which was to earth. The central rods could be connected to a sensitive quadrant electrometer.

The cylinder was covered with a thick layer of felt, and placed inside a metal box filled with cotton-wool, in order to keep temperature conditions as steady as possible.

In order to carry a sufficient quantity of emanation into the half cylinder, A, it was necessary to slightly heat the radium. The slide, S, was closed, and the side tubes

opened. A slow current of dry air from a gas bag, passed through a platinum tube, in which a small quantity of a radium compound was placed. The emanation was carried with the air into the cylinder, A. When a sufficient quantity had been introduced, as tested by the electrometer, the current of air was stopped. The side tubes were closed by fine capillary tubes. These prevented any appreciable loss of gas due to diffusion, but served to keep pressure of gas inside A at pressure of outside air. The three entrance tubes into the cylinder, shown in the figure, were for the purpose of initially mixing the emanation and gas as uniformly as possible.

After standing for several hours to make temperature conditions steady, the slide was opened, and the emanation began to diffuse into the tube B.



The current through the tubes A and B was measured by an electrometer, with suitable capacity in parallel, at regular intervals. Initially there is no current in B, but after the opening of the slide, the amount in A decreased and the amount in B steadily increased. After several hours the amount in each half is nearly the same, showing that the emanation is nearly uniformly diffused throughout the cylinder.

It can be readily shown that if—

K = coefficient of diffusion of the emanation into air.

f = duration of diffusion experiments in secs.

a = total length of cylinder.

S = amount of emanation in tube A at end of diffusion.

S_2 = amount of emanation in tube B at end of diffusion, then—

$$\frac{S_1 - S_2}{S_1 + S_2} = \frac{8}{\pi^2} \left\{ e^{-\frac{\pi^2 K t}{a^2}} + \frac{1}{9} e^{-\frac{\pi^2 K t}{a^2}} + \&c. \right\}$$

(See Stefan and Loschmidt, *Berichte Wien. Akad.*,
lxiii., 1871).

From this equation K can be determined, if S_1 and S_2 are known.

An uncertainty, however, arises, in estimating S_1 and S_2 for the rate of leak in A and B is made up of the current due to emanation alone, and the current produced in the gas by the excited radio-activity on the electrodes. As the amount of excited radio-activity increases with the time, the ratio of the current due to the emanation and to the excited radiation varies with the time allowed for diffusion. The ratio of the current due to the excited radiation can be determined by removing the central electrode, and finding the amount of current immediately after the introduction of a new electrode.

When the emanation is allowed to diffuse for half-an-hour, the current due to excited radio-activity was about 0.4 of the whole.

The calculated value of K was found to be about 20 per cent greater when the correction for the amount of excited radio-activity was applied.

The value of K deduced from the experiments was found to be between 0.08 and 0.15. All the later observations gave a value about 0.08.

This variation in the value of K deduced from the experiments is not altogether due to errors of experiment, the values obtained at first with a new specimen of radium were in all cases higher than when it had been laid by for several months. It appears as if the emanation were not simple in character, and that part of the emanation first given off was of lower molecular weight than that emitted after several months' exposure to the air. Further experiments are now being carried out to see if

the radium emanation undergoes a progressive change with time. For the purpose of comparison, we will now give a few of the coefficients of interdiffusion of gases, compiled from Landolt and Bernstein's tables:—

Gas or vapour.	Coefficient of diffusion into air.	Molecular weight.
Water vapour	0.198	18
Carbonic acid gas	0.142	44
Alcohol	0.101	46
Ether	0.077	74

In the above table we see that the coefficient of interdiffusion follows the inverse order of the molecular weights. In cases of the simpler gases it has been shown experimentally that the coefficient of interdiffusion is approximately inversely proportional to the square root of the product of the molecular weight. If we apply these considerations to the emanations ($K = 0.08$ to 0.15) we see that it is a gas or a vapour of molecular weight (allowing a wide margin) probably lying between 40 and 100. These numbers exclude the possibility of the substance being a vapour of radium, for it has already been shown by M. and Mme. Curie that the atomic weight of radium is greater than that of barium. We must therefore conclude that the emanation is in reality a heavy radio-active vapour or gas.

On account of the rapid decay of the radiating power of thorium emanations, it is not possible to determine its coefficients of diffusion in the same way; but special experiments show that it diffuses rapidly, and is also probably gaseous in character. The physical properties of these emanations or gases are most remarkable. The radium emanation not only continues for long intervals to be a source of radiation which is apparently similar in character to easily absorbed Röntgen rays, but in some way manufactures from itself a positively charged substance, which travels to the negative electrode and becomes a source of secondary radio-activity.—*Transactions of the Royal Society of Canada*, Series 2, vii., p. 21.

ESTIMATION OF TITANIUM.

By GEO. B. WATERHOUSE,
Bursar of the Royal Commissioners, Exhibition of 1851.

TITANIUM is an element that seems to have offered great difficulty to steel works' chemists. Although many processes have been submitted, there has not yet been one sufficiently short and accurate to be applied to working-day uses. It is hoped that the following process will provide for this need.

In looking over the various gravimetric methods suggested, it is at once seen that three things are common to almost all:—

1. Precipitation, by boiling, from largely diluted solutions.
2. Fusion with sodium or potassium carbonate.
3. Fusion with acid potassium sulphate.

Precipitation by simply long-continued boiling from solutions is, however, seldom complete, and the precipitate is contaminated with aluminium, silicon, phosphorus, and ferric salts, if these are present. The boiling also occupies a considerable time, and the precipitate is very liable to stick pertinaciously to the sides of the beaker. Boiling, then, in this way is an undesirable method of precipitating if another can be found. Titanium may be precipitated from solutions by ammonium hydrate—a fact made use of by Tosh (CHEMICAL NEWS, vol. xvi., p. 168), by Moissan (CHEMICAL NEWS, vol. lxxi., p. 103), and by others. But for the precipitate to be pure the titanium in solution must be separated completely from iron, aluminium, and other elements.

But, by boiling the solution, having previously eliminated all free acid, except about 1 per cent, with sodium acetate and 10 to 15 per cent glacial acetic acid, the whole of the titanium is precipitated after a brisk and short boiling, along with any silica and phosphorus present. Ferric salts must be removed, as they hinder the precipitation.

Fusion with sodium or potassium carbonate does not, as is stated, always render the whole of the silica soluble, but often along with the titanium, which is all insoluble, some of the silica is found. Phosphorus, however, is completely soluble as sodium or potassium phosphate.

Some processes, as Morgan's (CHEMICAL NEWS, vol. lxxv., p. 134), rely on the assumption that titanium in acid solutions (with the presence of sufficient phosphoric acid) is all rendered insoluble after baking as a phospho-titanate, but often some is still soluble, which is, of course, unaccounted for.

Gravimetric Estimation of Titanium in Steels or Pig-irons.

Weigh out 5 grms. of drillings into a 20-oz. beaker. Add 50 c.c. of strong hydrochloric acid solution. Heat gently until the steel is dissolved; then boil briskly and evaporate to dryness; bake, with a strong final heating. Remove from the plate, cool, and add enough strong hydrochloric to thoroughly saturate the dry chlorides, about 20 c.c. Heat for a few minutes, then add about 70 c.c. water, and boil until all the chloride of iron is dissolved. Filter through a small paper, and wash until entirely free from iron with a little warm 1:1 hydrochloric and cold water. Save the precipitate.

Place the filtrate in a 20-oz. beaker, make the volume up to about 150 c.c.; without heating add, little by little, dilute liquid ammonia until the acid is neutralised and there is a faint precipitate. Clear this precipitate with a few drops of hydrochloric; then add slowly about 50 c.c. of a 1:5 sodium sulphate solution. If a precipitate forms, or a dark colour persists, add a little dilute sulphuric acid until it is removed.

When the iron is in the ferrous condition, as seen by the colour, heat, and as it begins to boil add 50 c.c. glacial acetic acid and a filtered solution of about 20 grms. pure sodic acetate which have been heated in a separate beaker. Boil briskly for fifteen minutes.

If necessary, allow any precipitate to settle a little, and

filter through a large double paper. Wash the precipitate well out of the beaker, and wash the paper well with hot water. Dry this and the previous precipitate.

When dry, ignite them in a deep 3-inch platinum dish until all graphite and filter-paper are burned away. Place this dish in a desiccator. When cool, intimately mix the precipitate with about 10 grms. of pure dry powdered sodium carbonate. Fuse the mixture in the covered dish over a gas blowpipe until it is quite liquid, at which condition it is maintained for several minutes.

When cold, the fusion is thoroughly extracted in about 150 c.c. hot water. The dish is washed and removed. Allow the precipitate to settle, and filter through a hardened paper. The beaker and precipitate are washed very well with hot water.

Cautiously spread out the filter-paper on a clock-glass, and wash the precipitate into the beaker. Any adhering precipitate is dissolved off by means of about 10 c.c. hydrochloric acid, heated in the platinum dish, and poured over the paper. Wash all the yellow tinge out of the paper. To the beaker containing the precipitate, acid, and washings, add about 10 c.c. dilute sulphuric acid.

Cover the beaker and boil briskly down until white SO_3 fumes are seen. Remove from the plate, cool, and dilute to about 50 c.c. Filter if necessary, washing the paper well.

Dilute the filtrate to about 150 c.c. Add dilute ammonia until a faint permanent precipitate is obtained. Re-dissolve this as before, but only add 20 c.c. of the sodium sulphite solution. When colourless, heat the solution to boiling and add sodic acetate and acetic acid as before. Boil well for fifteen minutes. Allow the precipitate to settle, and filter through a large double paper. Wash the paper well round the edges with hot water. Dry as usual, and ignite in a weighed platinum crucible. The increase in weight is TiO_2 containing 60.97 per cent titanium.

To verify the above process, a standard solution of pure TiO_2 was made in the following way:—

Reputed pure titanic acid was taken, ignited strongly, and fused with an excess of sodium carbonate. The fusion was extracted, the precipitate filtered off, dissolved in hydrochloric and sulphuric, and evaporated to low bulk to separate SiO_2 . The titanium in the filtrate was precipitated by boiling with sodic acetate and acetic, filtered, washed, and ignited.

One grm. of the pure TiO_2 was then taken, fused with an excess of sodium carbonate, and the fusion extracted in sulphuric acid, about 2:1. The dish was washed and removed, and the clear solution transferred to a 120 c.c. flask and diluted to the mark.

Known quantities of this solution were introduced to different weights of pure iron, and the following results obtained:—

Weight of iron taken.	C.c. added.	Theoretical weight of precipitate.	Weight obtained.	Theoretical percentage.	Percentage obtained.
Grms.		Grm.			
5	1.0	0.0083	0.0084, 0.0086	0.1016	0.102, 0.103
4	2.5	0.0207	0.0209, 0.0212	0.317	0.318, 0.323
5	6.0	0.0500	0.0501, 0.0508	0.6097	0.610, 0.615
2	4.1	0.0341	0.0346	1.041	1.064
1	4.0	0.0333	0.0334	2.020	2.036

As it was also desirable to judge the influence of other elements on the process, a mean of 1 per cent of the following elements was introduced in such a form that they could go into solution, and the following results obtained:—

Weight of iron taken.	C.c. added.	Percentage of foreign elements.	Theoretical percentage of titanium.	Percentage obtained.
Grms.				
2	4.0	1 per cent Cr	1.016	0.980
2	4.0	1 " Al	1.016	1.018
2	4.0	1 " Ni	1.016	0.994
2	4.0	1.1 " W	1.016	1.012
2	4.0	1.2 " Mo	1.016	1.001
2	4.0	1.1 " V	1.016	1.048

Though the last result is a little high, the theoretical and practical weights of precipitate are very near, *i.e.*,—

Theoretical 0.0333 grm.
Weight found 0.0345 "

As a check on the solution, 4 c.c. were taken and the Ti precipitated with dilute ammonia, filtered off, washed, and weighed after ignition :—

Theoretical weight .. 0.0333 grm.
Weight found 0.033 "

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, *Metropolis Water Act*, 1871.

London, April 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us during the month, all were found to be clear, bright, and well filtered.

The deficit of rain still continues; the amount measured at Oxford during the month was 1.20 inches, the average fall is 1.47 inches; this makes a deficit of 0.27 inch, which added to the previous one of 2.27 inches gives a total deficit for the first three months of this year of 2.54 inches, or 47.4 per cent on the thirty-five years' average.

Our bacteriological examinations of 484 samples have given the results recorded in the following table; we have also examined 40 other samples, from special stand-pipes, wells, &c., making a total of 524 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 22 samples) ..	336
New River, filtered (mean of 116 samples) ..	13
Thames, unfiltered (mean of 24 samples) ..	2013
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 268 samples)	28
Ditto ditto highest	292
Ditto ditto lowest	0
River Lea, unfiltered (mean of 22 samples) ..	710
River Lea, from the East London Company's clear-water wells (mean of 31 samples) ..	12

Of the 415 samples of impounded and filtered water supplied to London and examined bacteriologically during the month, 20 samples, or 4.8 per cent, were sterile. Eight samples contained more than 150 microbes, while seventeen samples, or 4.0 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the seventeen excess samples was 166, against a corresponding

mean of 143 in nine excess samples during February. Thus it appears that the mean bacterial quality is not quite so high as it was last month. This must not be interpreted, however, as inferring that the majority of the London Companies were distributing less effectively filtered water; because a temporary falling off in the efficiency of a filter bed by any one Company is sufficient to increase the average of the whole, so as to produce a deteriorated mean result, such as we see this month on comparing the figures with those of last month.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

ON THE USE OF SALICYLATE OF SODIUM FOR THE ESTIMATION OF MIXTURES OF TERPENIC ALCOHOLS AND OF THEIR ETHERS.

By G. DARZENS and P. ARMINGEAT.

IN the October number of the *Bulletin Scientifique et Industriel*, MM. Charabot and Hébert published a paper entitled "Researches on the Mechanism of Etherification in Plants," in which they described a very simple method for the estimation of a mixture of terpenic alcohols and ethers.

This method depends on the solubility of these alcohols in a 50 per cent solution of salicylate of sodium, which dissolves neither their ethers nor their terpenes.

We were ourselves at that time occupied with this curious property of the salicylate, more especially with regard to the commercial purification of terpenic alcohols; but we also perceived that the simplicity of this process was only deceiving, and that it did not lead even to an approximate result.

We think it worth while to publish our results, as the proposed method of analysis can only lead to grave misconceptions if used without due warning.

We operated on mixtures of linalol, geraniol, rhodinol, and their acetic ethers, first making a mixture of one of these alcohols with its acetic ether, a mixture of which we accurately determined the coefficient of saponification, by which we were able to tell its proportion of ether. We then treated this mixture with four times its volume of 50 per cent salicylate of sodium; after twenty-four hours, the insoluble portion was decanted, and the solution of salicylate was precipitated by an excess of water, to recover the part dissolved. We then determined the coefficient of saponification of each of these portions.

We found that in every case the part dissolved contained large proportions of ether, as can be seen in the following table, which gives a summary of our experiments:—

Mixtures.	Part insoluble in the 50 per cent salicylate of sodium.		Part soluble in the 50 per cent salicylate of sodium.	
	Coeff. of saponification.	Ether per cent.	Coeff. of saponification.	Ether per cent.
Nature of the mixtures.				
Geraniol and acetate of geranyl ..	116	40.6	110	38.5
Linalol and acetate of linalyl ..	98.2	34.4	116.3	40.7
Rhodinol and acetate of rhodinyll ..	126	45	85	29
			The mixture was completely soluble.	

This result, which is rather deceiving, should not cause any surprise, as it agrees very well with our knowledge

of the properties of solutions. The following is the explanation:—

The solubility of the terpenic alcohols in salicylate of sodium at 50 per cent is not a chemical phenomenon, but simply a physical one; an occurrence which is better accounted for by phenomena of capillarity and thermodynamics than by chemical combination.

Thus we see that *ether being miscible, in all proportions, in its generating terpenic alcohol*, should also dissolve in the alcoholic solution in the salicylate; this solution being only a simple physical mixture must play a part in the properties of its constituents.

To prevent there being any doubt remaining as to this solubility of the ethers, and the interpretation we have put upon it, we have confirmed it directly by the following experiment:—

A solution of 10 c.c. of rhodinol in 40 c.c. of 50 per cent salicylate of sodium was prepared; then, by means of a graduated burette, acetate of rhodiny was added; this dissolved *instantly*.

By operating carefully and slowly, we were able to dissolve as much as 20 c.c. of acetic ether.

A moment, however, arrives when one drop of ether separates the mixture into two layers, as M. Duclaux observed with his mixtures. This limit of proportion is a function of the temperature at which the experiment is carried out, which further complicates the matter.

What we have stated with regard to mixtures of alcohols and ethers, also applies to mixtures of alcohols and terpenes.

A direct experiment finally showed us that we cannot depend on the salicylate to extract the terpenic alcohols from a natural essence containing alcohols.

An essence of geranium from Bourbon, having a coefficient of saponification of 72.9, was shaken up with four times its volume of a 50 per cent solution of salicylate of sodium. The recovered soluble portion had a coefficient of saponification of 64.2.

In publishing these remarks we in no way contradict the conclusions arrived at by M.M. Charabot and Hébert; it would be bold to assert that the salicylate of sodium process could never be of use in experienced hands when warned of the danger, and in certain cases where precision is not of great consequence it might be of considerable service.—*Bull. Soc. Chim.*, Series 3, vol. xxv., No. 24.

THE CEMENTATION OF IRON BY SILICON.

By P. LEBEAU.

In his experiments on silicide of iron, SiFe_2 , M. Moissan observed that the combination of silicon with iron could be effected before the fusion of either one or the other of these elements. He heated cylinders of soft iron packed in crystals of silicon, at the temperature of a good forge. Under these conditions the metalloid was not fused; however, the cylinders of iron, although they kept their shape, were transformed into silicide of iron, even to the axis of the cylinder. They contained 2 per cent of combined silicon.

We have recently had occasion to observe a similar fact, but one produced at much lower temperatures, and which causes this action of silicon on iron to appear very like the cementation of the same metal by carbon.

If we heat an intimate mixture of reduced iron and very finely divided silicon to 950° *in vacuo*, or in a current of hydrogen, the combination between these two metals takes place at a temperature very far from that of their fusing points.

The mixture of iron and silicon, which was compressed into the form of small cylinders, was found not to have changed its shape; it had acquired a greater solidity, but, as before, presented a spongy appearance and a dull tarnished fracture. When treated with nitric or hydro-

chloric acid, it dissolved without leaving any residue; all the silicon had entered into combination.

With a view to ascertaining whether this facility of combination could be attributed only to the state of division of the materials employed, we heated under the same conditions a small parallelepiped of soft iron, one of whose faces was polished and on which we simply laid a few crystals of silicon. After heating for five or six hours at the same temperature, we examined this polished surface. We were able to see with the naked eye that each crystal had left a trace of the image of its face adhering to the iron; the contours were slightly shadowy.

Similar facts were observed with nickel and cobalt.

We propose to examine this cementation of iron and other metals by silicon in a more thorough manner, notably to see if the presence of certain gases, such as nitrogen or carbonic oxide, would not influence the action.

Further, we may be able to apply it to the metallographic study of the metallic compounds of silicon.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 3.

THE ACTION OF SULPHURETTED HYDROGEN ON BROMIDE OF BORON.

By A. STOCK and O. POPFENBERG.

SULPHURETTED hydrogen does not act on chloride of boron in the cold; the action only commences on the chloride of boron fumes at a temperature above 250° , and at a dull red heat a certain amount of impure sulphide of boron is formed, contaminated with chloride. Thermochemical facts enable us to foresee a better result with bromide of boron, and, in fact, we find that the reaction takes place in the cold, giving a white body in the form of beautiful crystals. As these latter permeate the whole of the liquid and interfere with the end of the reaction, it is found to be more convenient to act with the sulphuretted hydrogen on a solution of bromide of boron in benzene or sulphide of carbon. The authors carried out their experiments in a small flask with a glass tube ground in with emery; the parts are fitted together and arranged so that the lower part can be easily removed if it becomes obstructed with a deposit of crystals, and also so that the bromide of boron and the solvent, when volatilised, can be condensed in a vertical condenser, and run back into the flask without interfering with the flow of sulphuretted hydrogen. The end of the escape tube is fitted with a drying tube filled with chloride of calcium. Fifty grms. of bromide of boron were dissolved in the same weight of sulphide of carbon, and well-dried sulphuretted hydrogen was passed through slowly.

In a short time torrents of HBr were given off; after forty-eight hours these fumes had almost ceased to appear. The action of the sulphuretted hydrogen was continued for six days and nights, when the operation was stopped and the liquid evaporated to dryness *in vacuo*. A well-crystallised body was then formed, which was re-crystallised in benzene or sulphide of carbon. This substance is a boric sulphhydrate, $\text{Bo}_2\text{S}_3 \cdot \text{H}_2\text{S}$ or $\text{Bo}_2\text{S}_3 \cdot \text{H}_2$, corresponding to metaboric acid; it crystallises in long white needles having the odour of sulphuretted hydrogen; it is quickly decomposed by water into BoO_3H_3 and H_2S ; soluble without decomposition, and re-crystallisable in benzene and sulphide of carbon (1 part in 5 of warm benzene, or sulphide of carbon, but very slightly soluble in this latter at -20°). It also reacts on alcohol, giving H_2S , and it appears to combine with ether; these reactions will be examined later on. By the action of heat at the ordinary temperature, this body loses sulphuretted hydrogen, the crystals effloresce and turn yellow, leaving sulphide of boron; this reaction is noticeable at 100° , and is complete at 300° . It is also preferable to work with sulphide of carbon rather than with benzenic solutions, as these latter, if heated to boiling-point, commence to give off a

little sulphide of boron. But in sealed tubes the sulphate melts at 120° ; at 140° we obtain a clear colourless liquid, which on cooling takes the form of a white crystalline mass, and is recovered unaltered. For the purpose of analysis this substance was treated with potash solution, the sulphur estimated in the form of Ag_2S , and the boron by polarimetry in the presence of mannite. Cryoscopic measurements of the benzenic solutions give the formula $\text{Bo}_2\text{S}_4\text{H}_2$ and not BoS_2H .—*Berichte*, vol. xxxiv., p. 399.

A NEW INVESTIGATION CONCERNING THE ATOMIC WEIGHT OF URANIUM.*

By THEODORE WILLIAM RICHARDS
and
BENJAMIN SHORES MERIGOLD.

(Continued from p. 188).

THE following method was found to fulfil the required conditions fairly well:—A quantity of the iodate was placed in a boat in a combustion tube, to one end of which was attached, by a ground glass joint, a weighed U-shaped tube. The free end of this tube was drawn out and fused to a smaller tube, which dipped into a solution of sulphurous acid. On heating the iodate in a stream of air and oxygen, the salt was decomposed, and the iodine was carried over and condensed in the U-tube, which was packed in ice. The small quantity of iodine vapour not condensed was collected in the sulphurous acid, and precipitated as silver iodide. The heating was continued for an hour after no more iodine could be seen coming off. The end of the U-tube was then sealed by fusing off the small tube, and the other end was closed by a ground glass stopper immediately after disconnecting from the combustion tube. In this way about 99 per cent of the total iodine was weighed directly as free iodine. Of course the small amount of iodine remaining in the oxide after ignition had to be determined separately, as already described. By this method the amount of iodine found was practically identical with that found by the sulphurous acid method.

In determining the iodine present in the oxide after ignition, it has been assumed that the iodine is present as iodide. Although it is hard to believe that at the temperature employed any of the iodine can exist as iodic acid, it is impossible to prove the point experimentally. The uncertainty in regard to this point renders the use of the method inadvisable where the greatest possible accuracy is desired. Hence none of these analyses have any significance as a basis for computing the atomic weight of uranium.

Besides the bright yellow, slightly soluble iodate, we prepared a paler yellow, more soluble, and more highly hydrated salt, which suffers transition quickly into the earlier compound at a high temperature, and more slowly at a low temperature. Double iodates with sodium and potassium were also prepared. Some of our observations were inconsistent with the published record concerning the subject; but in spite of our desire to clear up the uncertainty and to study the rather interesting transition phenomena, we abandoned the iodates because none of them gave promise of a precise basis for the determination of the desired atomic weight.

The next compound investigated was the oxalate, which has the composition $\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$. Owing to the comparatively slight solubility of this compound it can be obtained in a state of great purity by a few crystallisations.

The best method of analysis is that of dry combustion, the carbon dioxide being absorbed in potash in the usual manner. The uranium is left in the combustion tube as the green oxide, U_3O_8 , and, consequently, can be com-

pared directly with the weight of carbon dioxide obtained. This obviates the necessity of using the weight of the oxalate as a factor in the calculation of the atomic weight, and so eliminates the error due to included water. As already mentioned, this method has been used by Ebelen and Péligot in their determination of the atomic weight of uranium. There is in this method a possible source of error, difficult of detection and correction, but none the less dangerous, in the possibility that the uranium oxide may after combustion still retain traces of carbon. Moreover, it became evident, after a few analyses had been made, that combustion analysis, as ordinarily conducted, is an exceedingly questionable method where great accuracy is desired. The great difficulty in obtaining absolute "blanks" is well known. Our experience amply confirmed the observations of Mabery ("Inaccuracies in the Determinations of Carbon and Hydrogen of Combustion," *Journ. Amer. Chem. Soc.*, 1898, xx., 510), Auchy (*Journ. Amer. Chem. Soc.*, 1898, xx., 243), and others in regard to the loss of water and possibly of carbon dioxide from the ordinary form of potash bulbs. We also found a single sulphuric acid tube entirely insufficient to absorb all the water. Clearly, then, if we were to use this method, an elaborate investigation of the form of apparatus, method of procedure, and limits of error, was absolutely imperative. The use of the oxalate, however, did not seem sufficiently promising to warrant the necessary expenditure of time.

After thus investigating the uranium compounds which seemed likely to furnish a suitable basis for an atomic weight determination, anhydrous uranous bromide, in spite of its disadvantages, seemed most likely to fulfil the necessary requirements. As already mentioned, this compound oxidises with the greatest ease on exposure to moist air. It was necessary, therefore, to devise apparatus which should preclude any possibility of bringing the sublimed bromide in contact with the air of the laboratory until it had been collected and weighed. After much experimenting with different forms of apparatus, the following method was adopted.

(To be continued).

NOTICES OF BOOKS.

Engineering Chemistry; a Practical Treatise for the Use of Analytical Chemists, Engineers, Iron-masters, Iron-founders, Students, and others. By H. JOSHUA PHILLIPS, F.I.C., F.C.S., &c. Third Edition, Revised and Enlarged. London: Crosby Lockwood and Son. 1902. Pp. 406.

THE second edition of this book, published in 1894, now being out of print, it has been found necessary to publish this the third edition, and the opportunity has been seized to make several important additions to both the text and the illustrations. Compared with the first edition of 1891 the work has been increased by more than 120 pages and about 30 new illustrations, while the contents have again been brought up-to-date.

The principal addition to the present issue is the fully illustrated section upon the microscopical examination of iron and steel, for the substance of which the author acknowledges his indebtedness to Mr. J. E. Stead, F.I.C. Other additions include particulars of Hampe's method for the estimation of oxygen in copper, Hehner's bromine thermal test for oils, the Pensky-Marten flash-point apparatus, Redwood's apparatus for testing air for inflammable vapour; the fluidimeter, an instrument designed by the author for ascertaining the fluidity or viscosity of several oils at the same time; the Home Office test for the determination of the stability of explosives, &c. These additions have considerably added to the value of the book, which we believe will be received with as much favour as the previous editions have been.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxvii., No. 14.

Primary Batteries; Their Theory, Construction, and Use. By W. R. COOPER, M.A., B.Sc. London: The Electrician Printing and Publishing Company, Ltd. Pp. 324.

PRIMARY batteries are, to say the least of it, disappointing; they have raised hopes of great possibilities, but the realisation of these hopes has been comparatively small. Two of the great drawbacks to them are that they are generally expensive and nearly always "messy." However, they have their uses, and the advance made in recent years is by no means small, and most readers will be surprised on looking through these pages at the large number of primary batteries that there really are.

Many important additions have been made of late to the theory of the voltaic cell, and a considerable number of pages have been devoted to this part of the subject.

With regard to the practical part of the subject the author's object has been to describe those batteries which are in general use, or of particular theoretical interest, rather than to include all known, or unknown, batteries whether they are good, bad, or indifferent.

A specially interesting and valuable feature of this book is the comparison of the various kinds of batteries, showing their capabilities, and the author has included a number of curves obtained experimentally during the past few years, and which enable such comparisons to be made.

The book is divided into twelve chapters; the earlier chapters deal with the simple voltaic element, local action, and polarisation (a very comforting word, which is often used to hide ignorance), and the theory of the voltaic cell. We then have an interesting chapter on non-chemical cells and thermopiles, followed by a practical chapter on testing cells.

The last five chapters are devoted each to a particular kind of battery, viz., one and two fluid cells, dry cells, standard cells, and carbon consuming cells. Owing to the importance of the subject, standard cells have been dealt with at some length. The first really successful standard cell was that introduced by Latimer Clark in 1873, and this, after certain modifications as to the treatment of the materials, was finally given a legal position in this country in 1894, and is now known as the Board of Trade Clarke Cell.

Chapter XII., on carbon consuming cells, and the commercial generation of electrical energy, is of interest, and the subject may possibly be of great importance in the future. One of the first difficulties to be contended with in this class of battery is that of getting the carbon into solution, and it is necessary that solution should take place by means of ions, and that the solution obtained should be an electrolyte. Unfortunately, carbon does not form salts, and when used as an anode in hydrochloric acid, although a chloride CCl_4 is formed, this product has none of the properties of a salt, and is, moreover, an insulator. The various attempts which have been made to solve this problem are interesting, but at the same time discouraging, and the difficulties to be overcome appear to preclude the possibility of commercial success, at least in the near future.

The Tutorial Physics. Volume IV. A Text-book of Magnetism and Electricity, with 170 Illustrations, and Numerous Examples. By R. WALLACE STEWART, D.Sc. (Lond.). Fifth Edition. London W. B. Clive, University Tutorial Press. 1902. Pp. 368.

THIS, the fifth edition of this book, follows closely on the fourth edition, which was published in 1899. The arrangement originally adopted remains unchanged; the book is divided into three parts, viz.:—Part I., Electrostatics; Part II., Magnetism; and Part III., Current Electricity; comprising eighteen chapters in all, with a further thirty-five pages of appendices, &c.

These publications are well known by now, and afford a great deal of help to students and candidates for the matriculation, intermediate science, and preliminary

scientific examinations of the University of London, and their appreciation of them is apparent.

CORRESPONDENCE.

ARSENITE OF SILVER.

To the Editor of the Chemical News.

SIR,—Your readers will all be glad to see Mr. J. A. Wanklyn's name again as that of a contributor to your columns. To me his communication (p. 181) has a special and personal interest, as proving that my remarkable sleep for a long term of years has an exact parallel in the experience of Mr. Wanklyn.

Mr. Wanklyn's contribution commences with the statement that the result of an analysis of the canary-yellow arsenite of silver, made recently in his laboratory, "astonished" him. His surprise was due to the fact that the analysis showed the compound to contain Ag_3 : As instead of Ag_2 : As, as Mr. Wanklyn expected.

It is true that the well-known yellow arsenite of silver is described as "the tetrargentous salt, $2\text{Ag}_2\text{O} \cdot \text{As}_2\text{O}_3$ " in vol. i. of "Watts' Dictionary of Chemistry," published in 1866. On the other hand, in the First Supplement to that work, published in 1872, the formula is given as Ag_3AsO_3 , and this is true also of Morley and Muir's edition, published in 1888.

I have consulted a number of "chemical text-books" published at different periods, and have met with no instance since 1861 in which the obsolete formula so long cherished by Mr. Wanklyn has been adopted. Even the English edition of "Gmelin," published in 1852, gives $3\text{AgO} \cdot \text{AsO}_3$ as the formula of the yellow precipitate produced on adding ammonio-nitrate of silver to a solution of arsenious oxide. Among the text-books giving Ag_3 : As are Miller, 1863; Noad, 1864; Bloxam, 1867; Thorpe, 1873; Roscoe and Schorlemmer, 1877; Valentin and Hodgkinson, 1880; Attfield, 1881; Haughton Gill, 1883; Prescott and Johnson, 1890; &c.

Mr. Wanklyn's observation was anticipated forty years since by Charles L. Bloxam, who, in a paper published in the *Journal of the Chemical Society* for 1862 confirmed Filhol's formula, Ag_3AsO_3 , and suggested the contamination of the precipitate with excess of arsenious acid as the probable cause of the erroneous formula attributed to the compound by Pasteur.—I am, &c.,

RIP VAN WINKLE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

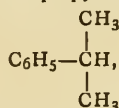
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxv., Nos. 18—19.

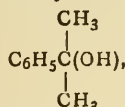
The Phenomena of Combustion in Industrial Furnaces.—O. Boudouard.—The author has already given the numerical results he obtained from the examination of the reaction $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$. He now shows how these facts enable him to definitely establish the theory of the different commercial operations, which have been based up to the present more or less on conjecture. The reaction $\text{CO}_2 + \text{C} = 2\text{CO}$ is a function of several important factors, and the best conditions for obtaining practical results are—(1) To have as high a temperature as possible, (2) the fuel must be very porous and finely divided, and (3) the speed of the current of gas should be as slow as possible, though if too slow the contact between the gas and the carbon will be too prolonged.

Estimation of Platinum and Iridium in Platinum Ores.—MM. Leidié and Quennessen.—Already inserted in full.

The Oxidation of the Homologues of Benzene.—Eyvind Boedtker.—The author undertook to show whether the careful oxidation of isopropylbenzene,—



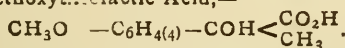
would give a phenyldimethylcarbinol,—



as expected by M. Friedel, and he finds that it is not only the group CH that is susceptible of fixing an atom of oxygen, but that the primary group CH_3 has the same property and apparently to the same degree.

The Electrolytic Oxidation of the Nitrotoluenes.—P. Pierron.—The electrolysis of orthonitrotoluene is conducted in a beaker heated on the water-bath and containing a porous pot of 150 c.c. capacity. The anode, formed of a strip of platinum, is placed inside, while a strip of nickel on the outside forms the cathode, plunged in sulphuric acid at 75 per cent. The mixture to be oxidised is placed in the porous pot, and the whole heated to 90° and electrolysed with a current of 1 ampère for fifteen hours. The acetic acid and the nitrotoluene of the mixture are carried off with the steam, and a tarry residue and a yellow liquor remain. This is exhausted with water, and the resulting liquid extracted with ether, which, on evaporation leaves a residue of needles fusible at 74° . The acetylated derivative is orthonitrobenzylic alcohol.

Paramethoxyarolactic Acid,—



—J. Bougault.—Five grms. of *p*-methoxyhydratropic acid are dissolved in 100 c.c. of water and treated with 12 c.c. of soda-lye. A solution is also made of 25 grms. of KMnO_4 in 500 c.c. of water and 25 c.c. of soda lye. The first solution is kept in a water-bath at $15-18^\circ$, and the KMnO_4 solution added by 100 c.c. at a time, about once an hour; the temperature must not be allowed to exceed 20° . It is then left for twelve hours after the last addition of permanganate, when it is found to have changed to a green colour. The manganate is destroyed by a slight excess of bisulphite of sodium and filtered. The solutions are evaporated down to about 100 c.c., neutralised with hydrochloric acid, and treated with a small excess of chloride of zinc. Paramethoxyarolactate of zinc is precipitated; this is collected and decomposed with dilute hydrochloric acid in the presence of ether. This latter, washed and evaporated, leaves the pure—or practically pure—acid. This acid is anhydrous, is slightly soluble in cold water, easily soluble in boiling water, alcohol, and ether; it melts at $129-130^\circ$; it decomposes slowly at 100° .

Methylene-3,4-Dioxyhydratropic Aldehyde and Acid.—J. Bougault.—This aldehyde is a colourless liquid, odourless when cold, but giving off very pungent fumes when heated. It is almost insoluble in water, but soluble in alcohol, ether, and chloroform. Its density at 15° is 1.203. It boils at $279-280^\circ$, and can be distilled at the ordinary pressure without decomposition. The acid is prepared by oxidising the aldehyde by means of oxide of silver in an alkaline solution. It forms anhydrous prismatic crystals, and fuses at 80° ; its isomer, methylenehydrocafeic acid, fuses at 84° . A solution of 1 in 500 of this acid, exactly neutralised with soda, forms salts when precipitated with nitrate of silver, sulphate of copper,

mercurous nitrate, and perchloride of iron; in the latter case the precipitate is re-dissolved on heating, and forms a red solution. The properties of these salts are described.

Phenylcarbazinate of Phenylhydrazine.—P. Freundler.—This substance is formed when the base is in the presence of an excess of CO_2 . The return depends essentially on the concentration, but cannot exceed 65 per cent of theory.

	Quantity used.	Vol. of CO_2 .	Wt. of dry carbazinate.
	Grms.	C.c.	Grms.
I.	20	300	6.5
II.	20	600	10
III.	20	1200	9
IV.	20	500	16

The theoretical return is 24 grms. It occurs in the form of a white crystalline powder, slightly soluble in cold water, decomposed by hot water and alcohol; it fuses at about 80° .

The Sulphonised Oxyazoic Colouring-matters and their Salts.—P. Sisley.—A long paper, not suitable for abstraction.

Hydrocinchonine.—E. Jungfleisch and E. Leger.—Already noticed.

Cinchonine.—E. Jungfleisch and E. Leger.—Already noticed.

Researches on the Mechanism of Etherification in Plants.—E. Charabot and A. Hébert.—Already noticed.

Some Essences of Thyme.—P. Jeancard and C. Satie.—Essences of thyme are estimated according to their proportion of phenols; it is generally considered that a pure essence should contain 25 to 30 per cent. The author, however, has examined pure essences in which the phenols varied from 5 to 60 per cent, and he has endeavoured to find the cause of these variations. To effect this he distilled the thyme with essence of ajowan, and gives a number of tabulated results. His principal conclusion is that the phenolic portions pass over at the end, and the results depend on the manner in which the distillation is carried out.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, April 29th, at three o'clock, Professor F. York Powell will begin a course of three lectures at the Royal Institution on "English Kings and Kingship"; on Thursday, May 1st, Mr. A. Smith Woodward will deliver the first of three lectures on "Recent Geological Discoveries"; and on Saturday, May 3rd, Professor Walter Raleigh commences a course of three lectures on "Poets and Poetry." The Friday Evening Discourse on May 2nd will be delivered by A. E. Tutton, Esq., on "Experimental Researches on the Constitution of Crystals"; and on May 9th by Professor J. Norman Collie, his subject being "Exploration and Climbing in the Canadian Rocky Mountains."

The New Volumes of the "Encyclopædia Britannica."—We understand that within a few weeks the first of the new volumes of the "Encyclopædia Britannica" will be published jointly by Messrs. A. and C. Black and *The Times*. Soon after *The Times* issued its reprint of the ninth edition, the project of publishing additional volumes was announced, and we are informed that this plan has been carried out in such a manner that the new publication will not only complete and bring up-to-date the ninth edition, thus forming in combination with the existing volumes the tenth edition of the "Encyclopædia Britannica," but will also constitute a distinctive and independent library of reference dealing with recent history and recent progress in all departments of knowledge. The editors-in-chief are Sir Donald Mackenzie Wallace, President Hadley, of Yale University,

and Mr. Hugh Chisholm. The contents will include more than 10,000 articles by more than 1000 contributors, 150 full-page plates, 125 coloured maps, and 2300 other illustrations, eleven volumes in all. The volumes will be published at, approximately, monthly intervals. We notice, with much surprise, that though departmental editors have been appointed for almost every branch of knowledge, such as Military Affairs, Theology, Mining, Botany, Astronomy, Electricity, Music, &c., there is no department for the most important science of all, Chemistry.

The Formation of Nitride of Magnesium by the Calcination of Magnesium in the Air.—W. Eidmann and L. Moeser.—M. Mallet has already announced (CHEM. NEWS, vol. xxxviii., p. 39) the formation of a considerable quantity of nitride during the incomplete combustion of magnesium in the air. The author has examined the conditions which gave the best results, the influence of foreign substances added to the powdered magnesium, that of temperature, and the access of air rendered more or less easy. If we gradually heat over a Bunsen flame, or better still, before the blowpipe, an iron crucible filled with magnesium filings, properly covered over, but having a very small hole pierced in the cover, we obtain, after heating for fifteen to thirty minutes, a greenish-yellow mass of Mg_3N_2 , up to 80 per cent of the amount of metal employed, covered with a grey layer of magnesium of variable thickness, itself covered by a layer of magnesia. —*Berichte*, vol. xxxiv., p. 390.

New Method for Determining the Molecular Weight of Ozone.—A. Ladenburg.—A bulb fitted with two taps is weighed, first full of oxygen as pure as possible, then full of ozonised oxygen, prepared with the same oxygen, and at about 8 per cent of ozone. All these operations must be carried out in a chamber in which the temperature does not vary more than a few tenths of a degree, and where the pressure remains constant. Let π be the difference between the two weights. The taps are opened in a vessel containing turpentine which absorbs the ozone; it is then weighed again, and, finally, the bulb is filled with the essence; these two last weights give the volume v of the ozone absorbed. Let d_1 and d be the specific gravities of pure ozone and oxygen, with regard to water, we get evidently $\pi = vd_1 - vd = v(d_1 - d)$. If ozone is ox , oxygen being o_2 , we have $\frac{d_1}{d} = \frac{x}{2}$, and, con-

sequently, $\pi = vd(\frac{x}{2} - 1)$, from which we get x . By this means, in five experiments, we found the values of x comprised between 2.83 and 3.14, and for the molecular weight of ozone the figures comprised between 45.3 and 50.4, or a mean of 47.78.—*Berichte*, vol. xxxiv., p. 631.

NOTES AND QUERIES.

*. * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Training and Prospects of Analytical Chemists.—As a chemistry teacher, I am sometimes asked by parents for information concerning the necessary training and prospects for lads desirous of becoming analytical chemists. Many of these are in a position to enable their sons to pursue their education with little or no salary until the age of twenty-five. Will you kindly give me the following information:—

- What would be the best or adequate course of instruction, with names of suitable institutions for pursuing such courses.
- The approximate cost of such instruction, excluding scholarships.
- The average salary for capable young men at the end of their course, in the following branches:—
 - (1) General analytical chemists.
 - (2) Works chemists (dyes, &c.).
 - (3) Assayers.

Books giving information on above would be of advantage to me.—H. T., B.Sc.

MEETINGS FOR THE WEEK.

MONDAY, 28th.—Society of Arts, 8. (Cantor Lectures). "Glass for Optical Instruments," by Richard T. Glazebrook, M.A., D.Sc., F.R.S.

TUESDAY, 29th.—Royal Institution, 3. "English Kings and Kingship," by Prof. F. York Powell, M.A., LL.D.

WEDNESDAY, 30th.—Chemical, 5.30. Ballot for the election of Fellows. "Preparation of Absolute Alcohol from Strong Spirit," "Vapour-pressures and Boiling-point of Mixed Liquids," and "Correction of the Boiling-points of Liquid from Observed to Normal Pressure," by S. Young. "Properties of Mixtures of the Lower Alcohols," "Properties of Mixtures of the Lower Alcohols with Benzene and with Benzene and Water," "Fractional Distillation as a Method of Quantitative Analysis," and "Vapour-pressures and Specific Volumes of Isopropyl Isobutyrate," by S. Young and E. C. Fortey. "Nitrogen Bromides containing the Propionyl Group," by F. D. Chattaway.

Society of Arts, 8. "The Timber Resources of the Australian Commonwealth," by Edward T. Scammell.

THURSDAY, May 1st.—Royal Institution, 3. "Recent Geological Discoveries," by A. Smith Woodward, LL.D., F.R.S.

Royal Institution, 5. Annual Meeting.

FRIDAY, 2nd.—Royal Institution, 9. "Experimental Researches on the Constitution of Crystals," by A. E. Tutton, B.Sc., F.R.S.

SATURDAY, 3rd.—Royal Institution, 3. "Poets and Poetry," by Prof. Walter Raleigh, M.A.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Incorporated by Royal Charter.

NOTICE IS HEREBY GIVEN that the next EXAMINATION of the INSTITUTE of CHEMISTRY, for persons desirous of qualifying themselves to be Public and Technical Analysts, will be held at 30, BLOOMSBURY SQUARE, LONDON, W.C., in JULY, 1902.

The Examinations are open only to such candidates as have complied with the Regulations.*

The Intermediate Examination will occupy at least four days, commencing on TUESDAY, JULY 22.

Examinations in the following branches of the Final Examination for the Associateship (A.I.C.) will extend over at least four days, and may commence on either JULY 15 or 22.

(a) Mineral Chemistry, (b) Metallurgical Chemistry, (c) Physical Chemistry, (d) Organic Chemistry, and (e) the Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy.

The Final Examination in the branch of Biological Chemistry will be held in OCTOBER.

Applications for admission to the July Examinations should be forwarded to the Registrar not later than TUESDAY, JUNE 10, 1902, on which day the list of candidates will be closed.

(By Order of the Council)

RICHARD B. PILCHER, Registrar and Secretary.

30, Bloomsbury Square, London, W.C., April, 1902.

* "The Regulations for the Admission of Students, Associates, and Fellows of the Institute of Chemistry" may be obtained from Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, E.C., price One Shilling.

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THE CHEMICAL NEWS.

Vol. LXXXV., No. 2214.

THE RADIO-ACTIVE ELEMENTS CONSIDERED AS EXAMPLES OF ELEMENTS UNDERGOING DECOMPOSITION AT ORDINARY TEMPERATURES. TOGETHER WITH A DISCUSSION OF THEIR RELATIONSHIP TO THE OTHER ELEMENTS.

PRELIMINARY NOTE.

By GEOFFREY MARTIN, B.Sc.(Lond.).

FOR many years there has been a general disposition to revive the ancient notion that all matter is composed of a common "protyle," and that the elements have been formed from it by a successive series of condensations.

And undoubted powerful experimental evidence has been furnished by the spectroscopic researches of Sir N. Lockyer, who believes the terrestrial elements are more or less completely dissociated into substances of a simple constitution at the high temperatures prevailing in the sun and stars. But what has hitherto been wanting is some experimental evidence that the elements do actually dissociate at temperatures attainable in the laboratory.

But it appears we have now this evidence, for the radio-active elements appear to be actually decomposing at ordinary temperatures.

Further, in all probability, this behaviour is not peculiar to the heavy radio-active elements, but occurs with every other element in the Periodic System at a suitable temperature range which differs for different elements. The only difference between the radio-active elements and the other elements of the Periodic System appears to be, that whereas in the case of the former elements this decomposition range commences at ordinary temperatures, in the case of elements of a lighter atomic weight the range occurs at higher temperatures.

In support of this view the following considerations may be urged:—A glance at Mendeleeff's periodic table will show the following gradual changes with atomic weight of the properties of the elements.

The lightest elements of any series are sharply defined and clear cut in their properties. They effect a condition of chemical repose or equilibrium in one particular state of combination, and this point of maximum stability is quite sharp and definite. In any other state of combination they are unstable. As, however, the atomic weight increases, this sharpness in combination becomes blurred, and the heavier elements of the group appear to be able to assume with ease more than one state of combination.

This shifting or blurring of the point of maximum stability of combination is always apparent with increase of atomic weight in any one group of the Periodic Table.

Now it is generally accepted that chemical combination is related to the presence of electrons in the atoms. Thus, a "ferrous" atom contains only two electrons, while, a "ferric" atom contains three. If we change the iron atom from the ferrous to the ferric state we lose one electron. Interpreting the preceding relation in the light of this, it would appear that an increase in the atomic weight of the elements of any one group leads to an increased tendency to change the number of electrons in the atoms. That is to say, there is a steady decrease, with increase of atomic weight, in the stability with which the electrons are retained by the atoms of the elements. And apparently with very heavy elements—like the radio-active elements—this instability has reached such a pitch that they are even now continually casting them

forth into space. So that the behaviour of the radio-active metals is only an extreme case of a tendency that exists among all the other elements of the Periodic System.

We have seen how increase of atomic weights brings about this condition of electrotonic instability among the elements. But exactly the same effect is brought about by an increase of temperature. Thus, at ordinary temperatures iron exists most stably in the ferric state. But the case is otherwise at a higher temperature. At these iron finds its state of maximum chemical repose in the ferrous state; ferric chloride and sulphate, for example, at higher temperatures decomposing to a greater or less extent into the corresponding ferrous compounds. And this behaviour is quite general among the other elements; the higher grade of combination invariably becoming more and more unstable, and the lower grade relatively more and more stable as the temperature increases.

Since every change of an elementary atom from a higher to a lower grade of combination is attended by the loss of one or more electrons, it is evident that the preceding behaviour is nothing less than the outward manifestation of the fact that, as the temperature increases, an element begins to attain a steadily increasing facility for parting with electrons usually retained by it at lower temperatures. And therefore there probably corresponds to each individual element a temperature range whereat this degree of electrotonic stability has become so marked that it spontaneously casts them forth.

When this occurs, the element is in a "radio-active" condition. So that the only difference between the so-called radio-active elements and ordinary elements is this—that ordinary temperatures are high enough to induce this condition in the heavy radio-active elements, whereas a higher temperature is necessary in the case of elements with lighter atomic weights—the temperature at which radio-activity is induced rapidly augmenting with decreasing atomic weights. According to this, radio-activity is a general condition of matter. Now, since the loss of electrons is attended with a loss of weight, it is evident that the radio-active elements are simply elements which, under given conditions of temperature and pressure, are suffering incipient decomposition, and that, further, this is only one particular example of a general decomposition which will occur among all the other elements at higher temperatures. In support of this view is the well-known fact that at high temperatures all substances become almost completely ionised. Even at ordinary temperatures it appears, from the experiments of Russell, that a great many bodies are slowly giving up electrons, and will affect a photographic plate in the dark, *e.g.*, zinc, and especially hydrogen peroxide (CHEMICAL NEWS, 1897, xxv., 302—396; 1898, lxxvii., 167—170).

The preceding is a mere speculation, but it is a speculation supported at every stage by experimental facts, as the following shows:—

(1). That an electric discharge shatters an atom, and reduces it to small particles, was shown experimentally by Sir W. Crookes many years ago. He called matter reduced to this fine state of division "Radiant Matter."

(2). That some of these small particles are electrons has been proved experimentally by Prof. J. J. Thomson and by Becquerel and others.

(3). That radio-active matter is at ordinary temperatures giving off electrons (and other particles?) has been proved experimentally by M. and Mme. Curie.

(4). That hot bodies actually give off electrons has strong experimental evidence to support it.

(a). It is an experimental fact that gases, which at ordinary temperatures are almost absolute non-conductors of electricity, when heated to incandescence acquire a conductivity which passes that of metals at ordinary temperatures; thus arguing for the presence of free electrons.

(b). Carbon also greatly increases in conductivity at high temperatures.

- (c). Hot bodies act in the same way as radio-active bodies in their power of discharging electroscopes. This was proved experimentally by Professor Worthington at the meeting of the British Association in 1888, and again quite recently by Mrs. Ayrton (*Nature*, February 27th, 1902, p. 390).
- (d). Hot metals can charge an electroscope in the same way that radio-active bodies can. This has also been experimentally proved by Mrs. Ayrton (*loc. cit.*).

The inference, therefore, is that a high temperature causes certain bodies to give off electrons in the same way that radio-active bodies do at ordinary temperatures; *i.e.*, that heat induces radio-activity in bodies.

The proof, however, is not quite complete until it is proved experimentally that the effects observed by Mrs. Ayrton are not due to the presence of air, but will take place with as great and even greater intensity in an absolute vacuum. It is to be hoped she will see her way to make experiments on these and other points, as the matter is of great theoretical importance, and if substantiated would experimentally prove the decomposition of elements by heat into electrons (and other inactive particles?).

(5). That heat does split up elements is shown, I believe, with the greatest precision by the experimental observations of Sir N. Lockyer on the spectra of different stars.

But what they are resolved into, whether into electrons and small particles of inactive matter as Crookes's experiments suggests, or into electrons alone, can only be decided by further experiment. In my opinion, I think it will be found that atoms when shattered give rise to three distinct kinds of particles:—

- Positively charged particles deviable in different degrees by magnetic and electrical influences.
- Negatively charged particles deviable in different degrees by magnetic and electrical influences.
- Inactive particles, composed of the unelectrified matter which composes the bulk of the atom. These particles, which may be very small indeed, would not be deviable by electric or magnetic influences.

Berlin University.
March 26, 1902.

THE MANUFACTURE OF OXIDE AND PEROXIDE OF BARIUM.

By R. HEINZ.

THE increasing importance of the oxides of barium has led to many methods being devised for the improvement of their manufacture. It is more especially the production of the monoxide that has occupied attention; it enables us, in fact, to prepare hydrate of baryta or the binoxide at a low price. Any new process which solves the question in a satisfactory manner must result in great activity in this branch of industry.

The methods for the manufacture of oxide of barium start from two principles, according to the use to which the product is to be put. If we wish to produce hydrate of baryta, the decomposition of the soluble salts of barium by an alkali cannot be considered as anything beyond a laboratory experiment. If we heat carbonate of baryta in the presence of superheated steam, it frequently happens that on the addition of carbon, we do not get satisfactory results, the decomposition being incomplete. It is only by treating sulphide of barium by oxide of zinc or by other metallic oxides that, for a long time past, large quantities of caustic baryta have been prepared; this method is, however, very inconvenient, and very ill-suited to working on the large scale. On the other hand, we can obtain a very pure oxide, and, thanks to its porosity, one very well

adapted to the preparation of the binoxide, by decomposing nitrate of barium at a high temperature in Hessian crucibles. The loss of nitric acid, however, makes the cost of the oxide thus prepared rather high. M. Wachtel (*Färber Zeit.*, 1900, II., 113; *Chem. Zeit. Rep.*, 1900, xxiv., 162) has given some very interesting general instructions for the manufacture of oxide and peroxide of barium.

The demand for peroxide has risen so rapidly that the resulting increase of production even cannot long remain as it is. However, as a general rule, no new factories have been started. In Italy, during the last few years, factories using the old nitrate method have been established, but with regeneration of the nitric acid; but it does not appear, up to the present, that any very advantageous results have been obtained. This method has also been tried in North America, but we have no authentic information as to the conditions of manufacture employed.

As for the peroxidation of the oxide, several new processes have been mentioned, differing slightly from those in use up to the present. These include the use of retorts arranged in various manners, of oblong or rectangular section, which can be filled and emptied easily, or muffle furnaces in several stages, so constructed that the whole furnace or each stage can be heated separately.

Thus we obtain regular heating, and the oxidation is effected regularly and easily. In practice compressed air is almost universally used for the oxidation.

With regard to the recovery of the nitric acid in the method by decomposing nitrate of barium, M. Wachtel's work already referred to may be consulted with advantage. It is claimed that 30 per cent of the total acid can be recovered (*Chem. Zeit.*, 1900, xxiv., 662), but this figure has not been verified.

As we remarked at the commencement of this article, the future has in store for us a new process of manufacture, which is a very great advance; it has been discovered at the cost of numerous and difficult experiments. The origin of this process lies in the sugar industry, more especially in the removal of sugar from molasses.

The deposits of strontianite and celestine are nearly exhausted, and new ones have not been discovered; on the other hand, it has been observed that the use of baryta completely removes the sugar from molasses, and that the product obtained is as good as that prepared by means of strontianite.

We must then, sooner or later, have recourse to baryta, and the present consumption of baryta in the sugar industry is fairly considerable. Efforts must therefore be made to establish a method for the manufacture of the oxide and hydrate of baryta which will satisfy the increasing demands which will arise. To begin with, we can only deal with carbonate of baryta, a product which can be obtained commercially in a state of great purity. Numerous attempts have been made to decompose this substance into its constituents, but all these processes are imperfect; either they are too expensive, or the decomposition is incomplete. M. Wachtel has already described several of these methods, so I shall only deal with those which he has passed over in silence.

M. Schulze proposes decomposing, by means of the electric arc, the residues from the treatment of the molasses, whether carbonates of barium or strontium. These products are mixed with carbon in the moist condition in which they are obtained, and the mass is well stirred during the fusion; there can be no doubt that a transformation takes place, and Schulze, in small experiments, obtained 90 per cent of the oxide of barium treated, but this was perhaps rather carbide of barium, if we take into consideration the quantity of acetylene gas given off on its solution in water. According to the inventor the cost would be very low, but from analogy we might form a very different opinion; to prepare 100 kilos. of oxide of barium, about 20 kilowatt-days would be required; this represents 20 marks, reckoning the kilowatt hour at 4 pfennigs, and then we are allowing nothing for

the wear and tear of the electrodes, nor the evaporation of the water present in the residues. Further, the apparatus has a stirrer which is supposed to be used at the temperature of the electric arc, about 3000°.

Naturally, the carbonic acid formed is recovered; as for the oxide of barium, it forms very compact and hard greenish-blue masses, which the inventor of the process regards as necessary for the preparation of the binoxide. The Schenk-Bradley and Borrows-Jacobs method is approximately of the same value as the preceding one; by fusing, in the electric furnace, a mixture of heavy spar and carbon we ought to obtain a mixture of oxide and sulphide of barium. The separation of the sulphide must follow on this costly operation. To these two methods we may add that of Limb, according to which carbide of barium is prepared by fusing a mixture of sulphide of barium and carbon with a metal or a metallic oxide in the electric furnace. The carbide is decomposed with boiling water; this gives baryta, acetylene, and a residue of a metallic sulphide. All these "electric" methods seem to be based on the idea that everything can be done by electricity. The losses of original material caused by the high temperature of the electric furnace are sufficient to diminish the returns by these methods very considerably. To this must be added the intense action of oxide of barium in fusion on the sides of the apparatus, and the extremely inconvenient carburised impurities which are always to be found.

We have still to mention the practical value of a French process which consists of decomposing chloride of barium by means of oxide of zinc at a white-red heat. Chloride of zinc should be formed, which is volatilised and re-used in the form of oxide, and porous oxide of barium. Leroy and Segay's process deserves more serious attention. Carbonate of barium is decomposed at 360° by sulphuretted hydrogen, and the dry sulphide formed is treated, below a red heat, with a current of steam; in this manner oxide of barium and sulphuretted hydrogen are formed. It still remains to be seen whether this method can be worked in a practical manner on the large scale.

There is only one recent process for the decomposition of carbonate of baryta which has been proved by practical results. It can be easily worked on the large scale, and is cheap. It has been the cause of numerous interesting observations, and has caused the discovery of such interesting details that the trouble and difficulty of its invention has been to a great extent recompensed. It is an interesting fact that witherite, the natural carbonate of baryta, gives up its carbonic acid much more readily than does the artificial carbonate; therefore it is employed in certain German manufactories in spite of its slightly higher price. The installation of the process only requires comparatively simple apparatus. Two conditions are of especially great importance, viz., the construction of the furnaces and the regulation of the calcination.

The lining of the furnace with basic refractory material should be done with the greatest care if we wish the furnace to last; ordinary magnesian bricks are not at all suitable for this purpose on account of their feeble resistance. The furnace should be heated by means of gas generators; this method being the only one enabling the necessary variations of temperature to be made, which are essential to the success of the calcination. It is of great importance to be able to vary the temperature rapidly, then to increase it progressively. If the temperature is raised too rapidly, or becomes too high, volatilisation, and consequently diminution of yield, takes place. By using 100 kilos. of carbonate and 125 kilos. of fuel, we obtain, on an average, 70 kilos. of oxide of barium.

In continuous working the calcination lasts about twelve hours, and no crucibles or similar apparatus are required. It is premature to give details of this process at present; it is simple in principle, but requires incessant watching. It is important to mention that by this method oxide of barium at 95 per cent can be obtained. The product

obtained is particularly suited for the preparation of a binoxide containing 90 per cent of BaO₂ free from cyanides and nitrites. The oxidation of this oxide is so easy that the peroxide can be obtained by the direct oxidation of carbonate of barium. The conduct of this operation on the large scale, however, offers certain mechanical difficulties; but the great advantage of this process is the joint production of the oxide and the binoxide of barium.

In the Hanover-Linden district a new installation has been erected at great expense for the manufacture of binoxide of barium from the oxide of barium made by the Bonnet, Ramel, Savigny, Giraud, and Marnas process. This method consists of calcining a mixture of carbon and carbonate of barium in Hessian crucible lined with paper, or some substance that will form carbon, and carrying it to 1100° or 1200°. This oxide does not seem very suitable for the production of the binoxide; according to our experiments it is a greenish-grey mass of bad appearance, and does not contain a sufficient proportion of oxygen. Our results were confirmed by the fact that this method has been abandoned after long and costly trials. The authors of this process themselves did not consider it suitable for the preparation of the binoxide, since it only gave a product suitable for this purpose after dehydration and calcining with carbon and hydrate of baryta.

The state of this industry as a whole is flourishing, and the consumption goes on increasing. At the present time France produces and exports a large quantity of hydrate of baryta, but Germany also supplies considerable quantities. On the other hand, this latter country is the principal producer of binoxide of barium. England is a serious competitor with the German manufacturers of the binoxide; other countries are of no importance in this respect, and obtain their supplies from England and Germany. The present total annual production of binoxide of barium may be put at 10,000 tons. It is especially by its production of peroxide of hydrogen that it finds many uses as a bleaching and oxidising agent.—*Chemiker Zeitung*, 1901, p. 199.

A NEW INVESTIGATION CONCERNING THE ATOMIC WEIGHT OF URANIUM.*

By THEODORE WILLIAM RICHARDS
and
BENJAMIN SHORES MERIGOLD.

(Continued from p. 201).

Preparation and Collection of Pure Uranous Bromide.

THE mixture of urano-uranic oxide and carbon was placed in a porcelain boat within the larger of two "telescoping" porcelain tubes. The portion of the tube containing the oxide was heated in a Fletcher furnace, and after thoroughly sweeping out the apparatus with dry nitrogen, a mixture of dry nitrogen and bromine vapour passed over the oxide. The sublimed bromide collected near the inner end of the smaller porcelain tube. The very efficient and elaborate desiccating apparatus which served so well in the work on the atomic weights of cobalt and nickel, was very kindly given by Dr. Baxter for use in this investigation.† This apparatus, with slight modifications, was used for drying the nitrogen and bromide, and was connected by a ground glass joint with the porcelain combustion tube.

With this apparatus traces of air diffused through the annular joint between the porcelain tubes, forming a coating of oxide on the inner tube.‡ In the case of

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxvii., No. 14.

† For a full description of this apparatus see *Proc. Amer. Acad. Arts. Sci.*, 1897, xxxiii., 124.

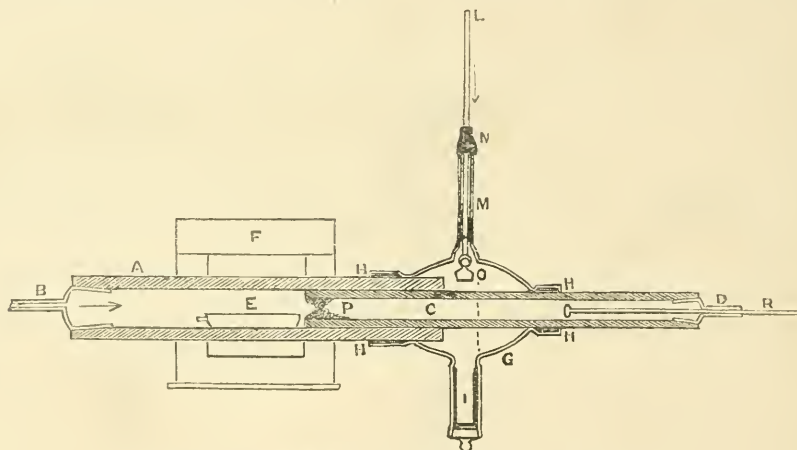
‡ In the case of cobalt and nickel this oxide was easily removed by subsequent treatment, but in the present case removal was impossible.

uranium, the oxide is found to be copiously mixed with the sublimate also. This diffusion of air takes place even when the outer end of the inner porcelain tube is nearly closed, thus making a considerable outward current within the tubes.

In order to obviate the difficulty and exclude air a glass jacket was slipped over the joint between the tubes. The construction and use of this jacket will be made clear by reference to the accompanying drawing.

The jacket was drawn down at the ends, so as to fit the porcelain tubes A and C as well as possible, and the spaces between the tubes and the jacket were packed tightly with asbestos-wool. This packing makes a joint sufficiently tight to withstand a pressure equal to that of 8 or 10 c.m. of water. The jacket was provided with a long tube, M, within which slid a second tube, L, connection being made by means of the short piece of rubber tubing, N. To the end of the inner tube was attached, by platinum wires, the stopper, O, of the weighing bottle. The outside diameter of L was very little less than the inside diameter of M, thus leaving very little space between the walls of the two tubes. For this reason, and also on account of the length of the tube M—about 15 c.m.—there was little danger of bromine diffusing up in sufficient quantities to attack the rubber connection, N. Even if this were the case there could be no possibility of contamination of the

heating in nitrogen, bromine vapour was passed in through B. During the first trials of the apparatus it was our practice to keep a slow current of nitrogen passing in at L during the sublimation. This kept the jacket entirely free of bromine, a very slow current of nitrogen being sufficient to keep any bromine from passing between the walls of the porcelain tubes. It was found, however, that traces of air diffused through the permeable asbestos packing, and were of course carried into the combustion tube by the current of nitrogen, forming on the inner tube a coating of oxide, and contaminating the sublimate. In order to avoid this, the nitrogen was shut off from L some time before turning on the bromine. After turning on the bromine, the jacket slowly filled with dilute bromine vapour. While the greater part of the sublimate collected within the inner tube, a little collected between the walls of the two tubes, almost sealing the annular space. This sublimate, which collected on the outside of the inner tube, is a valuable indicator of the condition of the sublimate within. In the presence of mere traces of oxygen the lustrous brown colour of the uranous bromide gives place to a dull yellow colour easily distinguishable. Comparatively small quantities of oxygen form a coating of black oxide. When the sublimation is conducted according to the method described, the outside of the inner tube is free from any traces of the supposed oxybromide or of



SECTION OF SUBLIMING AND BOTTLING APPARATUS.

A, Outer porcelain tube fitted with ground-glass joint; B; C, inner porcelain tube with ground-glass stopper; D; E, boat containing oxide and carbon; F, furnace; G, glass jacket; H, H, H, H, packing of asbestos-wool; I, weighing bottle; L, tube for admitting nitrogen, sliding within tube M through rubber connection N, and carrying at its end stopper O of weighing bottle; R, rod for removing sublimate.

sublimate thereby, since there was always a constant outward pressure of bromine during the sublimation. The outer end of L was connected with the nitrogen supply of the desiccating apparatus. All glass joints and stop-cocks were lubricated with syrupy phosphoric acid.

The method of procedure was as follows:—In the porcelain boat, E, was placed an intimate mixture of urano-uranic oxide and pure carbon, the carbon being about 20 per cent of the weight of the mixture, thus insuring a large excess of carbon. The apparatus was then thoroughly swept out by nitrogen, which enters at B and L simultaneously. After the air was completely expelled, the combustion tube was gradually raised to a high temperature by the blast lamp. Heating in a current of nitrogen was then continued for three hours at least, sometimes longer, in order to insure complete removal of all traces of air and moisture. During this and subsequent operations, the outlet of the stopper, D, of the inner tube was nearly closed by asbestos-wool, thus maintaining a constant and considerable pressure within the apparatus, and hindering the diffusion of air. After this preliminary

oxide, thus showing that no appreciable quantity of moist air could have reached the innermost portions of the sublimate. The best proof of the purity of the sublimate is of course found in the agreement of analyses of substance formed under various conditions of bromine supply.

After the bromine had been run for about one and a-half hours, the sublimate was cooled for three hours in a current of nitrogen. When the tubes were thoroughly cold, nitrogen was finally passed into the jacket through L, in order to sweep out any traces of bromine that might still remain. The inner tube, containing the sublimate, was then carefully drawn out until the inner end reached a position over the mouth of the weighing bottle, indicated in the diagram by the dotted line. This can be done without seriously disturbing the asbestos packing, a rapid current of perfectly dry nitrogen being admitted meanwhile through L. By means of the glass rod, R, the sublimate was pushed out of the tube, and dropped into the weighing bottle, I. The tube, L, carrying the stopper, was then pushed down and the stopper inserted. The stopper was held by the platinum wires so lightly that

after pushing it into place the tube, L, could be withdrawn, leaving the stopper inserted in the bottle.

Thus uranous bromide was sublimed, collected, and bottled up in an atmosphere of dry nitrogen ready for weighing, without once coming in contact with the air of the laboratory. That the apparatus is effective for the purpose intended, and capable of producing material of constant composition, was shown by the first rough analyses of uranous bromide, which yielded 57.41, 57.41, and 57.42 per cent bromine respectively. These analyses were made with material that had not been purified, but served to show the constancy of composition of the sublimate; for not only was the length of time occupied in the sublimation varied, but in one case the sublimate was cooled in bromine instead of in nitrogen. Of course if an appreciable amount of an oxygen compound were formed, by diffusion of air or moisture, there would almost certainly be discrepancies in the results, since it is hardly conceivable that under the varying conditions exactly the same quantities of oxy-salt should be formed each time.

Because the specific gravity of uranous bromide was unknown, the following determinations were made:—2.0328 grms. of the salt displaced on one occasion 0.3332 grm. of kerosene at 21°, and at another trial 0.3322 grm. The kerosene had been re-distilled, and only the high boiling portion was used. The density of the kerosene at 21°, referred to water at 4°, was 0.7919. Hence the specific gravity of the uranous bromide was (1) 4.830 and (2) 4.846, giving as the mean 4.838. This value was used in reducing the observed weights of bromide to the vacuum standard.

During the weighing in the final analyses, the bromide of uranium was still surrounded by an atmosphere of pure dry nitrogen in the tightly stoppered weighing bottle. Since this bottle had been full of dry air when it was first weighed, a small correction had to be applied on this account. The difference in weight between 6.70 c.c. (the interior volume of the weighing bottle) of air and the same volume of nitrogen at 20° C. is 0.000265 grm. Of this nitrogen a grm. of uranous bromide displaced

$\frac{1}{4.84} = 0.206$ c.c., or 0.24 m.grm., while the brass weights

used in weighing the bromide displaced 0.145 m.grm. of air. Hence in vacuum a grm. of uranous bromide would weigh $0.265 + 0.24 - 0.145 = 0.36$ m.grm. more than the observed weight, while 2 grms. would weigh $0.265 + 2(0.24 - 0.145) = 0.46$ more than the observed weight. All the weights given in the tables are corrected in this way to the vacuum standard.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

ANNUAL GENERAL MEETING, *March 26th*, 1902.

Prof. J. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

DR. HENRY and Mr. RAMAGE were appointed scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT, in beginning his Address, said that he had the agreeable duty of congratulating the Fellows on the continued and ever increasing prosperity of the Society.

The numerical strength of the Society was 2335 on March 28th, 1901. Since that date 163 Fellows had been elected, and 3 had been reinstated by the Council, making a gross total of 2501. Of these, 32 had withdrawn, 25 had been removed for non-payment of two annual subscriptions, and 21 had died.

The actual number of Fellows to date was therefore 2423, the highest number yet reached, and the number of Foreign Members was 32.

The following Fellows have died:—F. J. Beale, J. H. Beckett, Henry Bird, Sir J. H. Gilbert, F.R.S., A. Hart-ridge, Alexander Hay, Lawrence Hislop, David Johnson, N. Leonard, H. G. Madan, Dr. Ira Moore, Dr. G. Harris Morris, John Paul, W. Shapleigh, Louis Siebold, Prof Maxwell Simpson, F.R.S., W. T. N. Spivey, W. Terrill, John Thomson, J. L. W. Thudichum, G. F. Wilson, F.R.S.

The most important test of the prosperity of the Society was, however to be found in the record of its work. In this respect also he had a favourable report to make. Since the last Anniversary, 181 communications had been made to the Society. Abstracts of all these had appeared in the *Proceedings*, whilst 139 had already been published in the *Transactions*. He ventured to think that the quality, generally, of the work presented was as high as in any previous year, and clearly indicated the continued enthusiasm and activity of the Fellows.

The *Transactions* for 1901 contained 146 memoirs, occupying 1411 pages; and the volume of the preceding year 127 memoirs occupying 1334 pages.

The volumes for 1901 contain 3754 abstracts of papers, published mainly in Continental journals, occupying 1496 pages, arranged as follows:—

PART I.			Pages.	No. of Abstracts.
Organic Chemistry	..	..	784	1530
PART II.				
General and Physical Chemistry				403
Inorganic Chemistry	..	..		376
Mineralogical Chemistry	..	..		169
Physiological Chemistry	..	..		363
Chemistry of Vegetable Physio- logy and Agriculture	..	..		306
Analytical Chemistry	..	..		607
			712	2224
Total in Parts I. and II.	..	..	1496	3574

The volume for 1901 contained a Memorial Lecture giving an account of the life-work of Rammelsberg. A set of the Memorial Lectures which had appeared up to the end of 1900 was issued in September last in a separate form.

The use of the Library by the Fellows continued to show their appreciation of it. 880 books had been borrowed, as against 810 during the corresponding period of last year. A large number of these were journals issued by post to Fellows resident in the country, and the Library Committee invited special attention to this development of the Society's usefulness. The additions to the Library comprised 153 books, 441 volumes of periodicals, and 33 pamphlets, as against 95 books, 327 volumes of periodicals, and 30 pamphlets during the corresponding period of last year.

It was desirable that the Society should have in the Library a copy of, at least, every work printed in English on chemical subjects to the end of the Eighteenth Century, and he would invite the co-operation of the Fellows in making the Library complete in this direction.

In the preparation of the new Library catalogue, the printing of which had been decided upon, advantage was taken of the opportunity to construct a new and convenient Card Catalogue, which, it was believed, would materially assist readers in making use of the Library.

It was his privilege to offer, on behalf of the Society, its warm congratulations to Dr. Schunck, to Mr. Lloyd Bullock, and to Dr. Francis, who this year have reached their sixtieth anniversary of admission to the Fellowship of the Society. He had pleasure to add that Mr. Buckton,

F.R.S., Mr. F. Claudet, and Mr. Darby have reached their Jubilee, and to them he would also convey its sincere congratulations.

Last year their illustrious senior Foreign Fellow, M. Berthelot, celebrated the fiftieth anniversary of his first scientific publication, and all countries united in expressing their admiration and respect for the veteran chemist. On behalf of the Society, he, with Dr. Gladstone and Professor Ramsay, presented a congratulatory address to M. Berthelot at the imposing function which was held in the Sorbonne on November 24th, 1901. This address had already been printed in the *Proceedings*.

During the year, the Society had joined in the celebration of the 450th anniversary of Glasgow University, and in the jubilee of Owens College, Manchester.

Considering the large number of Fellows now in the Society, the mortality is small; nevertheless, this year they had to regret the loss of 21 Fellows. This melancholy list includes the name of Sir Henry Gilbert, Past-President of this Society, and one ever devoted to its welfare. His immense work, carried out with Sir John Lawes, laid the scientific foundation of British Agriculture, and serves as the model on which all future researches must proceed. The Society was fully represented on the sad occasion when Sir Henry Gilbert was interred, and its representatives laid a wreath on his grave, while later on the Council passed a vote of condolence with his mourning relatives. In a short time, he hoped, a full obituary notice would be published by one far more competent to undertake it than he. Dr. Maxwell Simpson is another of those passed away from amongst us, full of years, leaving memories of good work well done, especially in synthetic chemistry, and of him and of the other Fellows whose life-work has closed records will also be shortly published.

Considerable discussion has taken place within the Society on the question of altering the day and hour of the Ordinary Meetings, which was raised in the address of his predecessor, Dr. Thorpe, last year. They had had two Extraordinary Meetings on this subject, and the outcome was the experiment now in operation, of trying alternate evening and afternoon meetings until the end of the present session. Until that experiment had been fairly made, the best course, obviously, was to suspend judgment on the question.

Grants amounting to £250 had been made from the Research Fund in aid of chemical investigations.

The remainder of the address dealt with certain aspects of the Periodic Law as modified by recent discovery.

Dr. GLADSTONE, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*.

Dr. THORPE, C.B., F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Prof. TILDEN, F.R.S., the Treasurer, in giving an account of the balance sheet, which he laid before the Society, duly audited, said:—

The receipts had been:—By admission fees and subscriptions, £4532; by sale of Journal and advertisements, £835 11s. 2d.; and by dividends on invested capital, £476 12s. 6d. The total receipts from all sources amounted to £5884 1s. 8d. The expenses had been:—On account of the Journal, £3233 0s. 2d.; on account of the *Proceedings*, £20 1s. 5d.; on account of the Library Catalogue, £42 14s. 4d.; on account of the Library, £429 15s. 5d.; House expenses, £239 19s. 1d. The total expenditure being £4913 10s. 6d.

The TREASURER, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. CHAPMAN.

Prof. H. B. DIXON, F.R.S., proposed a vote of thanks to the Treasurer, Secretaries, and Council.

Dr. HEWITT seconded the motion, which was unanimously adopted.

Prof. MELDOLA, F.R.S., responded.

The scrutators having presented their report to the President, he declared that the following had been duly elected:—

President—J. Emerson Reynolds, Sc.D., M.D., V.P.R.S.

Vice-Presidents who have filled the office of President—

Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; J. Dewar, M.A., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., LL.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—E. Divers, M.D., D.Sc., F.R.S.; P. F. Frankland, LL.D., F.R.S.; H. McLeod, F.R.S.; R. Meldola, F.R.S.; H. A. Miers, D.Sc., F.R.S.; T. Stevenson, M.D.

Secretaries—W. R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary—W. Ramsay, LL.D., F.R.S.

Treasurer—W. A. Tilden, D.Sc., F.R.S.

Other Members of Council—H. B. Baker, M.A.; F. D. Chattaway, Ph.D., D.Sc.; F. Clowes, D.Sc.; J. J. Dobbie, M.A., D.Sc.; A. E. Dixon, M.D.; M. O. Forster, Ph.D., D.Sc.; A. Harden, M.Sc., Ph.D.; J. Lewkowsitch, Ph.D.; J. E. Marsh, M.A.; S. U. Pickering, M.A., F.R.S.; J. A. Voelcker, Ph.D.; J. Walker, D.Sc., F.R.S.

Extra Meeting, March 26th, 1902.

Prof. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

This meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

Professor J. H. VAN 'T HOFF, F.R.S., delivered the

Raoult Memorial Lecture.

François Marie Raoult was born on May 10th, 1830, at Fournes, in the Department of Nord. When he went to Paris to pursue his studies he had neither fortune nor patronage to assist him, so had to struggle to find means to keep himself. His first paper, published in 1853, contained observations on the transport of electrolytes by the galvanic current and on electrical endosmosis. In 1853 he was appointed "Aspirant répétiteur" in the Rheims Lycée, in 1855 "Régent de Physique" in the college at St. D.é, after which he was again at Rheims, and in 1860 at Bar-le-Duc, employing his spare time in working for his degree of *Licencié ès-Sciences Physiques*. In 1862, he proceeded to Sens, where, amidst adverse material surroundings, he prepared his thesis on *Électromotive Force*, for which in 1863 he obtained in Paris the degree of *Docteur ès-Sciences Physiques*.

The work of Raoult may be divided into three distinct parts: the physical, the chemical, and the physico-chemical. His career as a physicist begins with the thesis above referred to, by which he was marked out as an accurate and independent investigator already in advance of his time by the conclusions he based on a careful examination of facts. In the first part of this research he measured and compared in the cells of the Daniell type the amount of heat due to the chemical action with that corresponding to the electrical work produced, and showed that they were by no means identical. The second part was devoted to the decompositions in the voltameter by the galvanic current, the thermal phenomena being especially studied. It was whilst carrying out his electro- and thermo-chemical investigations that Raoult entered the *Faculté des Sciences de Grenoble* in 1867 as "chargé du cours de Chimie," being promoted in 1870 to the Chair of Chemistry, which he occupied until his death last year.

From this time forward a change is visible in the direc-

tion of Raoult's work, which now became of a more purely chemical kind, the problems still being looked at from the physical point of view. These problems included the examination of the gas from a "fontaine ardente," which he showed to be merely methane, the proof of presence of copper and zinc as normal constituents of the human liver, the inverting action of light on sugar. He showed that the presence of carbon dioxide in air diminished the production of carbon dioxide in the lungs, but that this effect was counteracted by the increased pulmonary action. His discovery of a basic calcium carbonate, $\text{CaCO}_3 \cdot \text{CaO}$, which acts like plaster-of-Paris on the addition of water, formed the subject of his last purely chemical paper. After this, he definitely enters upon that line of research which he has made peculiarly his own, and in which he persevered until his death.

His first paper on freezing-points was published in 1878 and was of a purely empirical nature, pointing out the proportionality existing between the lowering of the freezing-point and that of vapour-pressure (or raising of boiling-point). Probably owing to the difficulty of determining the strength of alcoholic liquors by means of their vapour-pressures or boiling-points, he tried their freezing-points. How this was related to practical applications is shown by the table appended to the paper, the liquids beginning with cider and ending with Marsala, the freezing-points varying from -2° to -10.1° , and corresponding fairly with the proportion of alcohol. From solutions of ethyl alcohol he passed to those of other alcohols, and thence to other organic compounds, giving his well-known table relating to twenty-nine substances. His conclusion was that the product of the depression of freezing-point of a solution containing 1 grm. of substance in 100 grms. of water multiplied by the molecular weight of the dissolved substance is a constant. Two further papers in 1882 extended the freezing-point law to solvents other than water, and he showed that each solvent has its own molecular constant which, probably by the formation of double molecules of the dissolved substance, may be reduced to half the normal value. This constant is proportional to the molecular weight of the solvent (M_1) and is on an average $\frac{K}{M_1} = 0.62$. From organic compounds

he passed to the more difficult cases of salt solutions, beginning with those of acids and bases, and finding that strong monobasic acids like hydrochloric acid and strong mono-acid bases like potassium hydroxide have a molecular depression of 37, whilst the weaker ones, like organic compounds, have only 18.5. He summed up his results thus:—"These facts prove that, in opposition to what I had admitted up till now, the general law does not apply to dissolved salts; on the contrary, they tend to indicate that it is applicable to the constituent radicles of the salts, almost as if these radicles were simply mixed in the solutions."

The early work of Raoult on voltaic cells was neglected, as it was much before its time, but his work on cryoscopy appeared just in the nick of time, and was soon warmly received everywhere. In 1892 he again took up his study of freezing-points which had been interrupted in 1884, but now from the point of view of the new theory of solutions, and showed that the molecular depressions of potassium chloride and sugar, as well as of sodium chloride and alcohol, were in accordance with the hypothesis of Arrhenius. In his summary of work in this direction, Raoult admitted all the conclusions of the theory of solutions, but as a thoroughly experimental investigator he objected to build upon that large but hypothetical generalisation known as the extended Law of Avogadro.

The relations existing between lowering of freezing-point and of vapour-pressures led Raoult to his tonometric work. He found (as Wüllner had already proved in some cases) that the ratio existing between the lowering of the pressure ($f-f'$), and the pressure itself (f), namely, $\frac{f-f'}{f}$,

the so-called *relative lowering* of pressure was independent of the temperature. His next step was to determine the values of the *molecular relative lowering*. He thus formulated what he found:—"One molecule of a non-volatile substance (salts excepted) dissolving in 100 molecules of any volatile liquid, diminishes the vapour pressure of that liquid by an almost constant fraction of its value, which is about 1.05 per cent." This conclusion at once brought him into connection with the theory of solutions, and Raoult himself says of it, in 1887, that "the agreement between experiment and theory is thus in all respects as complete as one can desire in such matters." In 1893, along with Recoura, he gave his most general and exact expression of the results of his vapour-pressure observations.

Raoult's constitution seems to have been a vigorous one, the only indication to the contrary being his resignation, in 1892, of an additional professorship which he had held. He ought to have retired in April, 1900, on account of his having reached the age limit for the tenure of his chair, but by special decision of the Trustees he remained in office "hors cadre," a very high honour, and a proof of his unbroken vigour at that time. In his last year, in two comprehensive papers, he summed up his views on Tonometry and on Cryoscopy; it was just in time, for, with practically no premonitory symptoms, he died on April 1st, 1901.

His character as a man may be read in his papers, in which he showed activity, patience, tenacity in pursuing an aim, as much eye for detail as for the vaster horizon, absolute independence of mind, criticising or admitting without bias views of others as well as his own, and testing both with the same calm conviction that the last word must rest with experiment.

Prof. ODLING, in proposing a vote of thanks to Prof. van't Hoff, said that he would not add a word to the appreciative, unaffected, and simple account of the work of Raoult. It was so lucid and complete that coming from any one it would have been of great interest, but in this case, coming from Prof. van't Hoff, it gave all the greater pleasure. Prof. van't Hoff's work in inorganic chemistry had exercised a very great influence on modern chemical doctrine for a quarter of a century; his work had excited a high degree of interest amongst English chemists, and to-night he had supplemented their acquaintance with his work by giving them the opportunity of making acquaintance with himself. The early work of Prof. van't Hoff did not, and very properly so, win its way without some opposition, which in certain Continental schools was unduly harsh. As with his theory of the chemical atom in space, so is it with the doctrine of osmotic pressure and the philosophy of solution. He could assure Prof. van't Hoff that in no country had these been received with greater favour than in this, in spite of opposition more vivacious than weighty. They were accepted if not as the final truth, if the truth at all, at any rate as running on all fours with the truth.

The vote of thanks was seconded by Prof. DEWAR, and supported by Sir WILLIAM HUGGINS, President of the Royal Society.

PHYSICAL SOCIETY.

Ordinary Meeting, April 25th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

DR. DAWSON TURNER exhibited and described a Mechanical Break for Induction Coils.

The use of induction coils in the production of Röntgen rays and in wireless telegraphy has made the construction of a suitable break a matter of importance. The ordinary break is unsuitable because of the wearing away at the point of contact, and there are objections to the use of mercurial breaks. The portable mechanical break which was shown by Dr. Dawson Turner consists of two metallic

rollers with their axes parallel, and kept in contact by a spring. One of the rollers has a cam attached to its spindle and can be made to rotate by means of a small electric motor. Once in each revolution the cam separates the rollers, thus making the break, and at the same time causing the second roller, which rides loose upon its axis, to turn about one-eighth of a revolution. As soon as the cam has passed the rollers are brought into contact by the spring, and the next break occurs at a different place. The wearing is thus distributed evenly over a large surface. The break is placed in a box containing alcohol or petroleum, and works best when rotating rapidly. An objection to the arrangement is the noise it makes when working. Some experiments were then shown on the discharge of electrified bodies by ultra-violet light. A disadvantage of the electric arc when used to furnish ultra-violet light for use in medicine is that the light is accompanied by heat, so that it is necessary to shield the patient from the heat without interfering with the passage of the light. A condenser spark between iron electrodes is useful because it gives a large amount of ultra-violet radiation without much heat. Dr. Turner showed that this light is capable of discharging bodies whether positively or negatively electrified. He then showed that glass and mica are opaque to the radiation, while pure rock salt is transparent.

Mr. WILSON NOBLE exhibited a Mechanical Break similar to the one already shown.

A roller and a disc, with their axes parallel, are placed in contact, and made to rotate in the same direction by a motor. Longitudinal slots are cut upon the surfaces of both, and the break occurs when a slot in the roller comes opposite a slot in the disc. Since the two are moving in opposite directions at their point of contact the break is very sudden. To vary the length of the break without altering the rate of rotation, the slot in the roller is wider at one end than the other, and the disc can be placed so as to touch the roller at any point of its length.

The CHAIRMAN said he knew of no metal which would withstand continual sparking without wearing, and suggested that breaks should be so designed that the parts affected by the sparking could easily be replaced. He asked if there was any difference in the wear of the two rollers. Referring to an experiment shown by Dr. Turner in which ultra-violet light discharged a positively electrified body much quicker than a negatively electrified one, he asked if this would be the case if the apparatus were surrounded by an earthed metallic screen.

Mr. WATSON suggested that the wearing of the edges in Mr. Wilson Noble's break might be lessened by filling the cavities with slate.

Mr. DUDDELL said that the worst substance for making contact pieces was carbon; then came zinc, brass, and copper, with platinum best. These were the results in air, but the effects in liquids were different. With rapidly moving contacts all metals are equally good, but in ordinary coils the contact pieces move slowly.

Prof. EVERETT said it was interesting that rock salt, which is very transparent to long waves, should also be transparent to very short waves.

Dr. DAWSON TURNER said that if the experiment referred to by the Chairman had been performed inside an earthed metallic screen the negatively electrified body would have been more quickly discharged.

Mr. R. S. WHIPPLE exhibited a Temperature Indicator for Use with Platinum Thermometers, in which readings are automatically reduced to the gas scale.

The instrument is very similar to the well-known Callendar and Griffiths temperature indicator, with the exception that it is so arranged that the readings obtained are automatically reduced to the gas scale, thus avoiding the necessity of applying a correction. It consists of a simple Wheatstone's bridge with equal ratio arms, the other arms being the thermometer and a long helical bridge wire together with the compensating leads. A

travelling contact is moved round the wire until a balance is obtained. The bridge wire is wound on an ebonite drum, on the outer surface of which a helix has been cut. The contact piece, which is connected electrically with the galvanometer, is carried from the inside of a cylinder fixed to a shaft. A white celluloid tube on which the scale is divided is fixed to the outer surface of the cylinder. A screw of the same pitch as the helix on the ebonite drum is cut on the shaft, so that by rotating the shaft the contact is caused to travel along the bridge wire, and at the same time the scale is carried past an index placed above it. The scale has been so constructed that the reading at the index gives directly the temperature of the thermometer reduced to the gas scale. The instrument reads from 0° to 1400° C.

Dr. CHREE asked the following questions:—Was not the instrument so constructed restricted to platinum thermometers of wire having a given specified value of δ ; if so, what was this value? Did the helical wire balance the entire resistance of the thermometer, or only the excess above the resistance at 0° C., and could the instrument measure temperatures below 0° C.? What error was likely to come in when measuring temperatures up to 1000° C. from changes in the resistance of the helical wire under the variations of atmospheric temperature to which it would be exposed in ordinary use? Would not there be some wear between the wire and the contact-piece?

Dr. HARKER asked what were the limits of the value of δ for wires now supplied for commercial purposes. He thought that the accumulation of dust between the contact-piece and the wire, due to continual scraping, was a more serious objection than the wearing away of the wire.

Mr. WHIPPLE said the scale was calculated for a value of $\delta = 1.5$. The value of δ seldom exceeded 1.52, and wire could be obtained with $\delta = 1.5$. The instrument shown was made to read from 0° C., but could be easily arranged to read below 0° C. The wearing between the contact-piece and bridge-wire was very slight.

Mr. S. A. F. WHITE read a "Note on the Compound Pendulum."

In the determination of the length of the equivalent simple pendulum for a compound pendulum whose form is a symmetrical bar and bob, with one fixed, one movable knife-edge, and no sliding weight, it is convenient to make the mass of the movable knife-edge small. In this case small displacements of this knife-edge will not materially alter the position of the centre of gravity or radius of gyration of the pendulum about an axis through its centre of gravity. The time of swing about the fixed knife-edge will therefore remain practically constant. The best determination of the correct position of the movable knife-edge for an equal time of oscillation will be given when, for the smallest displacement of this knife-edge, there is the greatest variation in the time of oscillation about it. The author has determined the position which makes $\frac{dt}{dh}$ a maximum, h being the distance of the axis of suspension from the centre of gravity.

He has also drawn the curve showing the relation between $\frac{dt}{dh}$ and h . The calculations have then been applied to the determination of the position of the movable knife-edge in a particular pendulum. The experimental value of the ratio of h to k deduced from this pendulum when the movable knife-edge is adjusted to its right position, agrees well with that predicted by the theory.

The author states that when the length of the equivalent simple pendulum is about a metre, it should be possible with a stop-watch reading to 0.2 second, to determine g to about 0.1 or 0.2 per cent. If the fixed knife-edge were made the movable knife-edge, the value of $\frac{dt}{dh}$ would be very large, but there would be difficulties in the

way of measuring the small time of swing and the small equivalent length.

Dr. CHREE said that the mathematical work might apply to either of two distinct problems. It might refer to the case of an ordinary pendulum with one movable knife-edge, the object sought being the particular position in which a given change in the period answered to the greatest movement of the knife-edge. The second case, the one which he supposed the author had in view, was that of a Kater pendulum, the object being to ascertain what design enabled the position of the movable knife-edge to be most accurately determined from the condition that the period about it should equal that about the fixed knife-edge. The author's reasons for neglecting the solution answering to a short pendulum of large moment of inertia did not appear mathematically complete, though they might be supported from physical considerations as to the relative accuracy of the determinations of g with long and with short pendulums.

Mr. WATSON said that, as a practical problem for students, the length was the most difficult thing to measure. The position of the movable knife-edge for strict equality of period could be deduced by interpolation from periods determined in two positions of the movable edge. In accurate work a light bob, equal in size to the heavy bob, might be placed upon the other end of the pendulum to keep the air friction constant.

The Society then adjourned until May 9th.

NOTICES OF BOOKS.

Calorimetry of Producer and Illuminating Gases. With Special Reference to Future Legislation. By JOHN F. SIMMANEE, Assoc.M.Inst.C.E., M.Inst.Mech.E. London: Walter King. Pp. 30.

THIS volume does not propose to deal in any way with the theoretical heat values of gases, but is intended to be a practical guide for the operator who desires to estimate, rapidly and accurately, their practical calorific effects in recognised units. It is obvious that for different tests to be comparable they must be carried out in a similar manner. This is done with regard to the illuminating power of coal-gas, but with gas calorimetry no such uniformity of working or of apparatus has hitherto been attempted, and it is with the object of effecting this that the present present code of instructions has been prepared.

In modern gas calorimetry the amount of heat imparted by the combustion of a given volume of gas to an ascertained quantity of water is the basis for estimating the calorific power of the gas.

The calorimeter is, briefly, a means of enveloping the flame in a shell of water which is regularly changed, and the temperatures of which before and after passing the instrument are accurately gauged, as is also the after-temperature of the products of combustion. The essential points of the test are:—

1. The accurate measurement and invariability of the gas flow.
2. The same as to the water.
3. The correct reading of the thermometers.
4. The obviation of any outside influences which might induce errors in the above.

These four principal points are considered in turn, and a number of useful hints are given to help in the satisfactory carrying out of the tests.

A detailed account of the tests then follows, in which most minute instructions are given, making it next to impossible for any one who reads this book to make a mistake. If it is pointed out that the most likely cause of difference between two operators is the "personal error"; this, however, can be entirely abolished by making the gas meter automatically measure the water as well, when the operator will only have the thermometers and the water-gauge to attend to.

The Year-Book of New South Wales. Compiled by the Editor of the "Year-book of Australia," for Circulation by the Agent-General in London. 1902. Pp. 168.

THIS book is compiled somewhat on the lines of the well-known Whitaker's Almanack, though on a much smaller scale. It contains a large amount of political, historical, and commercial information, which bears ample evidence of the increased industrial importance of the country. So rapid has this development been that it is found necessary to have a specially appointed resident official in London for each of the Australian Colonies, these gentlemen being called the Agents-General. They are intrusted with all external business, especially that of a financial character, but it is also a portion of their duties to supply those desiring it with any information procurable respecting their several Colonies.

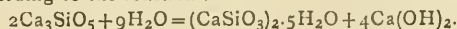
In these pages we find a good account of the mineral resources of the Colony, accompanied by a large coloured map showing the districts in which the various minerals are met with. The water supply is also fully dealt with, and many interesting particulars are given. Sydney appears to have an exceptionally large supply; the main storage reservoir at Prospect, about twenty-two miles from the town, has a gross capacity of 11,392,713,000 gallons, and an available capacity of 7,324,343,000 gallons; this reservoir is formed by a dam 84.7 ft. high, 30 ft. wide on the top, and 7400 ft. long, giving a water surface of 1261 acres, or nearly two square miles.

The important progress that the mining industry of New South Wales has made is apparent when looking through the statistics given. Every decade from 1831-40 to 1891-1900 shows a large and growing increase, the total value to the end of 1900 being £140,635,533, among which we notice noble opals £456,599, and diamonds £55,535, besides the well known large returns of gold, silver, copper, tin, coal, &c.

The Chemical and Physical Examination of Portland Cement. By RICHARD K. MEADE, B.S., Instructor in Chemistry in Lafayette College. Easton, Pa.: The Chemical Publishing Company. 1901. Pp. 183.

IN preparing this manual the author has kept in view the possibility that many cement manufacturing companies are employing young men fresh from technical schools whose college training may be excellent, but whose practical experience is usually limited to a few analyses, while their knowledge of making the physical tests is in all probability even less; for this reason both the chemical and physical examination of cements have been explained very fully and with abundance of detail.

Tricalcium silicate is the essential element of Portland cement, in which it occurs in cubical crystals; in this compound the lime and silica bear the ratio of 2.78 to 1. Le Chatelier concluded from his researches that the tricalcium silicate when mixed with water reacts to form a hydrated monocalcium silicate and calcium hydroxide, according to the reaction:—



The calcium hydroxide then probably reacts further upon the calcium aluminate of the cement, forming hydrated, basic, calcium aluminate, $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 12\text{H}_2\text{O}$. The "hardening" of cements is due to the first reaction, but the formation of the hydrated basic calcium aluminate probably exerts a marked influence on the "setting."

On the other hand, Messrs. S. B. and W. B. Newberry arrived at different conclusions, viz., that a correctly balanced Portland cement should be made as follows:—Per cent of lime = per cent of silica $\times 2.8$ + per cent of alumina $\times 1.1$. The ratio between the silica and alumina on the one hand and the lime on the other is termed the "hydraulic index."

The principal constituents to be determined in the analysis of cements are the silica, ferric oxide, alumina, lime, magnesia, and carbonic acid. Analytically, cements lie on the one side between limestones and marls, which

are easily decomposed by dilute hydrochloric acid, and on the other, clays and refractory silicates requiring fusion with alkaline carbonates for their decomposition. Different methods for all these estimations are given, both gravimetric and volumetric, besides rapid methods for the analysis of cement mixtures, slurry, &c.

The value of a cement depends on its physical properties, more especially its setting power, tensile strength, and soundness; a quick-setting cement, one setting in less than half-an-hour, is preferable for submarine work, while for most purposes, where sufficient time will be given the cement to harden before being brought into use, a slow-setting cement usually answers better.

While in actual work cement is never used in such a way as to subject it to tensile stress, still the test of the tensile strength is the most convenient, as the ratio between the tensile and compressive strength of a cement has been found to be a fairly constant one, various methods of applying this test are fully described. The book, which is well adapted to be of practical use, closes with a number of reference tables and an index.

A College Text-book of Chemistry. By IRA REMSEN. London: Macmillan and Co., Ltd. 1901.

This book is intended to be intermediate in difficulty between the "Introduction to the Study of Chemistry" and the "Inorganic Chemistry" of this series. According to the old familiar method, the several elements, grouped according to Lothar Meyer's system of natural families, are studied successively in detail; thus there is nothing new in the arrangement of the book; on the other hand, it is probably hardly necessary to say that the text is accurate and thorough. The subject-matter of every chapter is illustrated by a few experiments, admirably described in all cases with a sufficiency, but not a superfluity, of detail; the suggestive questions addressed to the student should fulfil their purpose of making him think of, and reason about, what he is doing; and we feel inclined to believe that if they fail in exciting and keeping alive his interest he will profit but little by the study of natural science. The first half of the book is devoted to the principal elements of families VII. to IV., and the compounds they form with one another. Chapters XXIII. and XXIV., which deal with the theory of chemical action and general considerations relating to the base-forming elements, admirably demonstrate the author's capabilities in the direction of lucid explanations and far-reaching generalisations. The rest of the book is occupied with the metallic elements and familiar compounds of carbon.

Beiträge zur Chemischen Physiologie und Pathologie. Edited by FRANZ HOFMEISTER. Band II., 1-3 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1902.

THE first paper of the March number of this journal deals with the effects of the addition of various substances upon the solidifying and melting-points of gelatin. The substances added were, firstly, single inorganic salts; secondly, two salts, either with or without common ions; thirdly, a mixture of an electrolyte and a non-electrolyte; and lastly, non-electrolytes. The results are graphically represented in fourteen curves. This paper is the first instalment of further communications concerning similar researches on albuminous bodies. The second paper, by Dr. Hugo Wiener, on the synthetic formation of uric acid in the animal body, contains a number of tables showing the influence of the addition of various organic substances either *per os* or subcutaneously on the formation of uric acid in birds and mammals respectively. The general result appears to be that the substances employed with a chain containing three carbon atoms up to propionic acid produce an increased formation of uric acid, while all substances with a chain of four carbon atoms up to β -oxybutyric acid have no effect.

In another of the eight articles contained in this number is discussed the occurrence in the pancreas of an enzyme, similar to zymase, which is capable of splitting up dextrose and forming carbon dioxide and alcohol. The question presents considerable difficulties when attacked experimentally, and the researches described appear to leave the matter still undecided.

Thermodynamique et Chimie. By P. DUHEM. Paris: Librairie Scientifique, A. Hermann. 1902.

IN the first five chapters of this work, which is intended for the use of chemists, the fundamental principles underlying chemical statics and dynamics are thoroughly examined and formulated, and an attempt is made to exclude as far as possible all references to higher algebra, so that the student who does not possess any considerable knowledge of mathematics will be able to follow the author's reasoning without difficulty. A special feature of the book is the great amount of attention paid to recent developments and applications of thermodynamics. If in places we feel that the importance of some of these applications is exaggerated, and that some of the views put forward are unduly biased, we are, nevertheless, conscious that Professor Duhem has conferred a real benefit on chemists generally by bringing his great knowledge of physics to bear upon the question of the simplification of the difficult subject of thermodynamics.

CORRESPONDENCE.

ARSENITE OF SILVER.

To the Editor of the Chemical News.

SIR,—Your correspondent "Rip van Winkle" asserts, in effect, that the composition of the canary-yellow arsenite of silver was finally settled by Bloxam's paper published forty years ago in the *Journal of the Chemical Society*. But careful examination of the literature of that period shows that Bloxam's paper, so far from clearing up the mystery of the composition of the canary-yellow, left that question in greater confusion than ever.

Before Bloxam's publication the canary-yellow was supposed to be one definite chemical substance, or, at any rate, to be of approximately uniform composition. Bloxam's paper imports a doubt.

There is only one complete analysis of any specimen of the canary-yellow, and the analytical figures lie about midway between the Pasteur formula and the Filhol formula. The figures are:—

AgO	..	..	..	..	..	..	..	74.77
As ₂ O ₃	..	..	..	..	..	..	..	25.88
100.65								

Bloxam's surmise as to the nature of that specimen of canary-yellow was that it consisted of Filhol's arsenite mixed with a quantity of arsenious acid.

To the filtrate from that specimen of the canary-yellow more solution of nitrate of silver was added, and also ammonia, and a further precipitation of canary-yellow took place. That second specimen of canary-yellow was not fully analysed, the only analytical figure being 22.19 per cent of As₂O₃. That figure accords with the Filhol formula, and would have been important if it had been associated with a concordant silver determination.

In the absence of the necessary silver determination it establishes nothing at all; inasmuch as the drop in percentage of As₂O₃ from 25.88 to 22.19 might have been due to deposit of saltpetre or nitrate of silver in the precipitate. In short, there was surmise when there might have been certainty; and Pasteur's erroneous composition of the canary-yellow arsenite was not rectified in the year 1862.

Under these circumstances we need not wonder that the Pasteur formula for the canary-yellow found its way into "Watts's Dictionary" in the year 1863, when the first volume was issued, and that it remained in possession of the field until the completion of the Dictionary in the year 1868. Neither need we wonder that so well-informed and so careful a chemist as Dittmar retained the Pasteur formula in one of his books issued in the year 1876.

In conclusion, I have to state that "Rip van Winkle's" assertion that my recently published work was anticipated by Bloxam is absolutely devoid of foundation.

In some very important aspects Bloxam's results are the very opposite of mine. Bloxam's canary-yellow was of variable composition.

In my hands the canary-yellow arsenite has exhibited the utmost constancy of composition.

In my paper there is a record of a complete analysis of the pure canary-yellow; in Bloxam's paper no such record is to be found.—I am, &c.,

J. ALFRED WANKLYN.

The Laboratory, New Malden Surrey.

April 27, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

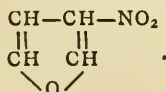
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 14, April 7, 1902.

A Type of the Compounds of Beryllium.—H. Lacombe.—The author succeeds in preparing homologues superior to beryllium acetate, $(C_2H_3O_2)_6Be_4O$; this latter substance being prepared last year. All the compounds obtained are of the type A_6Be_4O , A representing the radicle of a fatty acid. He has not yet succeeded in preparing salts of the type A_6Be_4O with strong mineral acids.

Constitution of the Chlorohydrines.—Marc Tiffeneau.—In 1875 Markovnikoff showed, contrary to Henry's assertions, that during the fixation of $ClOH$ on to propylene, the oxyhydride takes the least number of hydrogen atoms on to the carbon, giving chlorohydrine, $CH_3-CHOH-CH_2Cl$. However, he attributes to isobutylene chlorohydrine the formula $\begin{matrix} CH_3 \\ | \\ CH_3 > CCl-CH_2OH \end{matrix}$, apparently showing that it is not possible to establish a general rule for the fixation of $ClOH$ on to the ethylenic carbides. The author now verifies Markovnikoff's rule that, during the fixation of $ClOH$ on to the ethylenic carbides, the oxyhydride always takes the least hydrogen on to its carbon atom.

Nitration of Furfurane, and a Derivative of Nitrosuccinic Aldehyde.—M. Marquis.—During the nitration of furfurane in acetic anhydride solution, the ring is opened, with formation of a monoacetate of nitrosuccinic aldehyde. Pyridine is able to act on this substance, closing the ring by raising the elements of acetic acid, and giving a nitrofurfurane whose constitution is evidently the following:—



The author proposes to next examine the aldehydic product of the action of water on nitrosuccinic acetate.

New Method of Preparation of Oxygen.—George F. Jaubert.—The peroxides of sodium and potassium are very rich in active oxygen; that is, oxygen which can easily be evolved in the gaseous state. Sodium peroxide contains 20.5 per cent, potassium 33.8 per cent of such oxygen. The author endeavours to utilise these bodies

for the industrial preparation of oxygen and facilitate its change into the latent state in a solid body susceptible of giving it up in the cold under the simple action of water. The sodium peroxide is made into blocks by simple compression after being mixed with the theoretical quantity of a soluble permanganate (Na, K, or Ca) or of a hypochlorite, the latter substance facilitating the decomposition of the hydrate of sodium peroxide which forms under the action of water and is stable in the cold. The oxygen obtained by such a method is interesting from several points of view, chiefly on account of the ease of formation, —an apparatus of the nature of Kipp's sufficing to prepare thousands of litres, —and also on account of the absolute purity of the oxygen prepared.

Classification and Atomic Weights of Neon, Argon, Krypton, and Xenon.—H. Wilde.—In a previous paper on the atomic weights of argon and helium, the author finds the position of argon amongst the elements comes near to nitrogen in the series $H \times 7n$, with an atomic weight 21. The elements recently discovered, neon, krypton, and xenon, entirely confirm the position and the atomic weight of argon in this table; and the most recent determinations of the densities of these new gases by Ramsay and Travers show that they belong to the series $H \times 7n$. The gaseous members of the series $H \times 7n$ are arranged in the following order:—Ne, 7; N, 14; Ar, 21; Kr, 42; Xe, 63.

MISCELLANEOUS.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Wednesday and Thursday, the 7th and 8th of May, 1902, commencing each day at 10.30 a.m.

Programme of Proceedings.

Wednesday, May 7th, at 10.30 a.m.—General Meeting of Members. The Council will present their Report for the year 1901. The Hon. Treasurer will present the Statement of Account for 1901. Scrutineers will be appointed for the examination of the Voting Papers. Election of Officers and Council. The Bessemer Gold Medal for 1902 will be presented to His Excellency F. A. Krupp, of Essen. A selection of Papers will be read and discussed.

At 7 p.m., Annual Dinner of the Institute in the Grand Hall of the Hotel Cecil.

Thursday, May 8th, at 10.30 a.m.—General Meeting of the Members at the Institution of Civil Engineers. The following is a list of the Papers that are expected to be submitted:—

Report by the Committee appointed to investigate the Nomenclature of Metallurgy.

"On a New Vacuum Tuyere for Blast Furnaces." By Horace Allen, London.

"On the Microstructure of Hardened Steel." By Prof. J. O. Arnold and A. McWilliam, Sheffield.

"On the Compression of Fuel before Coking." By J. H. Darby, Brymbo.

"On Gas from Wood for Use in the Manufacture of Steel." By James Douglas, LL.D., New York.

"On a Combined Blast-furnace and Open-hearth Process." By P. Eyermann, Benrath, near Düsseldorf.

"On the Physical and Chemical Properties of Carbon in the Hearth of the Blast Furnace." By W. J. Foster, Darlaston.

"On the Sulphur Contents of Slags and other Metallurgical Products." By Baron H. von Jüptner, Donawitz, Austria.

"On the Elimination of Silicon in the Acid Open-hearth Furnace." By A. McWilliam, Sheffield, and W. H. Hatfield, Sheffield.

"Report on Research Work carried out during the Past Year." By J. A. Mathews, Ph.D., New York (Andrew Carnegie Research Scholar).

"On the Iron Ore of Brazil." By H. Kilburn Scott, Rio de Janeiro.

"On the Recovery of By-products in Coking." By J. Thiry, London.

"On Brinell's Researches on the Influence of Chemical Composition on the Soundness of Steel Ingots." By Axel Wahlberg, Stockholm.

The Autumn Meeting of the Institute will be held in Düsseldorf on September 2nd and following days.

"Mechanical Refrigeration."—Messrs. Whittaker and Co. announce that they have in the press and will shortly publish in their Specialist Series a work entitled "Mechanical Refrigeration." The volume, which is by Mr. Hal Williams, A.M.I.Mech.E., will deal with the whole field of ice making and cold-storage, and while designed for the use of those technically interested in the industry, and is in all respects a practical book, is an attempt to express in simple language the principles regulating the action of refrigerating machinery, and the latest and most up-to-date practice in its application.

MEETINGS FOR THE WEEK.

MONDAY, 5th.—Society of Arts, 8. (Cantor Lectures). "Glass for Optical Instruments," by Richard T. Glazebrook, M.A., D.Sc., F.R.S.

--- Royal Institution, 5. General Monthly Meeting.

--- Society of Chemical Industry, 8. "On the Mixed Carbides of Manganese and Calcium," by J. S. Brame and Prof. Vivian B. Lewes. "Dangerous Chemical Substances," by Oscar Guttman, F.I.C.

TUESDAY, 6th.—Royal Institution, 3. "English Kings and Kingship," by Prof. F. York Powell, M.A., LL.D.

--- Society of Arts, 8. "The Printing of Modern Illustrated or Decorated Books," by Charles T. Jacobi.

WEDNESDAY, 7th.—Society of Arts, 8. "Origin and History of Carriages," by Albert Chancellor, J.P.

--- Iron and Steel Institute. Annual Meeting, 10.30 a.m. Dinner, 7 p.m.

THURSDAY, 8th.—Iron and Steel Institute. General Meeting, 10.30 a.m.

--- Royal Institution, 3. "Recent Geological Discoveries," by A. Smith Woodward, LL.D., F.R.S.

--- Society of Arts, 4.30. "Past and Present connection of England with the Persian Gulf," by Thomas Jewell Bennett.

FRIDAY, 9th.—Royal Institution, 9. "Exploration and Climbing in the Canadian Rocky Mountains," by Prof. J. Norman Collie, Ph.D., F.R.S.

SATURDAY, 10th.—Royal Institution, 3. "Poets and Poetry," by Prof. Walter Raleigh, M.A.

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THE CHEMICAL NEWS

VOL. LXXXV., No. 2215.

FURTHER NOTE ON MINERALS OCCURRING IN AUSTRALIAN BAT GUANO.

By R. W. EMERSON MACIVOR, F.I.C., &c.

MR. L. FLETCHER, F.R.S., the distinguished head of the Mineralogical Department of the British Museum, writes me a courteous letter, in which he points out that the name Müllerite which I proposed to give to the new ammonium-magnesium phosphate, $Mg(NH_4)_2H_2(PO_4)_2 \cdot 4H_2O$, described in my recent paper in the CHEMICAL NEWS (vol. lxxxv., p. 182), has been used lately by Zambonini (*Zeit. Kryst. Min.*, 1899, vol. xxxii., p. 157) for a mineral having the composition $Fe_2O_3 \cdot 3SiO_2 \cdot 2H_2O$; and also that it had previously been used for a "Krennerite-like mineral."

"I am afraid," says Mr. Fletcher, "that Zambonini's description has the priority as regards this assignation to a species with determined character (specific). The confusion is regrettable, and perhaps the best and simplest plan would be for you to give a new name in substitution for the one given so long ago."

In compliance with this suggestion, and to prevent all future confusion, I have now decided to call this interesting mineral Schertalite, in honour of an old master, Prof. Arnulf Schertal, late of Freiberg, Saxony.

The Laboratory,
29, Fenchurch Street, E.C.

AN INFRA-GASEOUS STATE OF MATTER.

By H. STANLEY.

IT is now about a quarter of a century since Sir William Crookes enunciated his theory of the ultra-gaseous state of existence of matter, and what he then termed "radiant matter" now poses as "electrons."

Suppose we have a gas confined in a cylinder fitted with a piston which will enable us to keep the pressure constant as we cool down the gas. Let this pressure be less than the critical pressure and greater than zero. Then let the temperature be speedily reduced to absolute zero.

Considering this in the light of Van der Waals's well known theorem, we have—

$$\left(p + \frac{a}{v^2}\right)(v - b) = 0.$$

Since, by hypothesis, the pressure is not zero, we must have—

$$v = b.$$

Now, at absolute zero, the molecules of a gas will be dormant as far as energy of translation is concerned, but there will still remain an attractive force between the molecules, viz.,—

$$\frac{a}{b^2}.$$

This force will be proportional to the product of atomic masses or some similar quantity, independent of temperature.

According to Van der Waals, b is four times, and according to O. E. Meyer $4\sqrt{2}$ times, the space occupied by the molecules. Now the heat developed by this attractive force will be measured by—

$$b_1 \int \frac{a}{b^3} db = a \left(\frac{1}{b_1} - \frac{1}{b_2} \right);$$

where b_1 is the quantity defined as above (i.e., a constant

times the volume of the molecules), and b_2 is the absolute volume of the molecules.

If we define the molecule as a cluster of quasi-Boscovich atoms of non-spherical shape (see Kelvin, *Phil. Mag.*, 1901), by their mutual attraction they will agglomerate irregularly, and in so doing will yield up heat according to the above expression. If, now, the pressure is increased till we reach a critical value, the molecules will assume a regular and definite position with respect to each other (i.e., condense). There is thus an intermediate or "infra-gaseous" state between the gas and liquid.

NOTE.—Since writing the above, I have read with interest Brinkworth and Martin's paper on a somewhat similar question ("The Heatless Condition of Matter," CHEMICAL NEWS, vol. lxxxv., p. 194). Is their "heat-point" the temperature at which the "infra-gaseous" state exists? as the heat developed, according to the foregoing equation, if not allowed to escape, would raise the temperature of the gas by a definite amount, which would vary with the nature of the gas.

Merchant Venturers' College,
Bristol, April, 1902.

THE ACTION OF SOME REAGENTS ON AMORPHOUS SILICON.

By P. LEBEAU.

WITH the object of deciding whether free silicon would be likely to be present in the products resulting from the attack of siliceous cast-iron by different compounds, we were led to examine the action of certain reagents on amorphous silicon.

Having only been able to find very scanty information on this subject, we thought it would be of interest to publish the results of our experiments.

As it seemed reasonable to admit that the free silicon existing in metallurgical products containing only a very small proportion of this metalloid would be in a very fine state of division, we made our experiments on the most finely-divided silicon we were able to prepare. For this purpose we separated, by means of levigation, the lightest portions of an amorphous silicon obtained by M. Vigouroux's method. The action of each reagent was examined in the following manner:—

A certain quantity of the thoroughly dried amorphous silicon was weighed out, and it was acted on by the liquids usually used for the attack of cast-iron, operating either in free air in a porcelain crucible, or in a conical Bohemian flask fitted with a cork and two glass tubes to allow the passage of a current of carbonic acid.

The duration of each experiment was about six hours, and the temperature was maintained at about 100°. At the end of this time the solution was poured on to a tared filter to collect the silicon, which was washed successively with hydrochloric acid at one-tenth per cent, then cold water, and finally with boiling water. The desiccation was effected in an oven at 80°. The following are the results obtained:—

Nature of the reagent.	Weight of silicon used.	Weight of silicon found	
		In free air.	In the current of CO ₂ .
	Grm.	Grm.	Grm.
Solution of cupric chloride at 10 per cent	0.200	0.203	0.2004
Solution of cupric sulphate at 10 per cent	0.200	0.2002	0.2012
Solution of CuCl ₂ + NH ₄ Cl at 10 per cent	0.200	0.1996	0.2008
Solution of CuCl ₂ + KCl at 10 per cent	0.200	0.2015	0.1998
Nitric acid with its own volume of H ₂ O	0.302	0.3015	—

Our experiment with nitric acid only confirmed the previous experiments of M. Vigouroux (*Ann. Chim. Phys.*, Series 7, vol. xii., p. 5) on the action of this liquid on silicon, which he mentioned in his paper on the properties of this metalloid.

We also used a ten per cent solution of chromic acid under the same conditions.

The silicon was weighed on a tared filter after the destruction of the chromic acid by hydrochloric acid and alcohol.

Weight of silicon used . . . 0.2372 grm.
Weight of silicon found. . . 0.2363 "

As in the attack of castings a ferrous or a ferric salt is produced, we thought it advisable to examine in the same way the action of a solution of ferric chloride and that of a solution of ferrous chloride.

	Weight of silicon used. Grm.	Weight of silicon found. Grm.
Ferric chloride at 10 per cent . .	0.3135	0.3133
Ferrous chloride at 10 per cent . .	0.229	0.2296

The result of all these experiments clearly shows the resistance of silicon, even when finely divided, to the reagents generally used for the attack of cast-iron and steels. We can thus be certain that its absence in the residues from these attacks arises from the fact that the silicon is present in combination and not in the free state.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 3.

ESTIMATION OF THE SILICON IN RICH FERRO-SILICONS BY MEANS OF PEROXIDE OF SODIUM.

By Dr. C. RAMORINO.

THE use of peroxide of sodium for the determination of silicon in rich ferro-silicons (50 per cent and over) has not yet been applied practically in laboratories, on account of the difficulty found in working with this compound. The reaction which takes place if we attempt directly to decompose a ferro-silicon rich in silicon and carbon by means of the peroxide is very violent, on account of the powerful exothermic reaction which takes place. Reduction occurs suddenly, accompanied by projections and perforation of the platinum crucible. On the other hand, the disaggregating reaction takes place very quietly and completely if we treat 0.5 grm. of the finely powdered ferro-silicon with 10 grms. of an intimate mixture of carbonate of sodium and potassium (Fresenius's formula, "Qualitative Analysis") with 1 grm. of powdered peroxide of sodium. This is heated slowly before the blow-pipe to prevent any projections. The decomposition is soon complete. After cooling on a plate of polished steel, it is treated with boiling water and then with dilute hydrochloric acid in a porcelain crucible. The platinum crucible is well washed and the solution evaporated to dryness on the water-bath, after adding 10 c.c. of nitric acid and 2 grms. of chlorate of potassium. It is then heated in the hot air oven to 110°, and taken up with 20 c.c. of pure hydrochloric acid and 200 c.c. of distilled water. After boiling, it is filtered on the filter-pump, washed with hot water, dried, and calcined in a muffle in a platinum crucible. Perfectly white silica is obtained, $\text{SiO}_2 \times 0.4667$ = silicon.

This method is most rapid with the very rich ferro-silicons, which are not attacked by acids, and it gives perfectly concordant results.

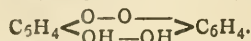
In the filtrate, the manganese can be estimated by the volumetric method with oxide of zinc and titrated permanganate, and also the sulphur by means of chloride of barium.—*Moniteur Scientifique*, vol. xvi., January, 1902.

CHARACTERISTIC REACTION OF PHENIC ACID.

By M. MANSEAU.

THE action of chlorine and bromine on phenols in alkaline solution, especially ammoniacal, is well known.

We further know that the direct oxidation of the phenols gives coloured bodies called quinones, having the property of being generally oxidisable and colourable, and of uniting, by the aid of reducing agents such as sulphurous acid, ferrous chloride, &c., with two atoms of hydrogen, giving hydroquinones, $\text{C}_6\text{H}_4(\text{OH})_2$, and, by incomplete reduction, the green hydroquinone or quinhydrone,—



It is to an oxidation of this character that we may apparently ascribe the reaction we have obtained while preparing a medicament, well known abroad under the name of "Hagner's olfactive," after a celebrated Polish doctor.

This medicament consists of a mixture of equal parts of carbolic acid, ammonia, tincture of iodine, and camphorated alcohol. It appears to be an excellent remedy for coryza. It suffices to breathe in the volatile principles (ammonia, camphor, and the phenolic ethers) which are given off to obtain rapid relief.

But what is interesting from the chemical point of view is this, that on adding the tincture of iodine to the mixture of carbolic acid and ammonia, a fleeting water-green colouration occurs, quickly disappearing, and leaving an absolutely colourless liquid. We have attempted to fix this reaction and make it persistent. For this purpose we placed, in a test-tube, a few crystals of pure carbolic acid, dissolved in 1 c.c. of alcohol; we then added a few drops of pure ammonia and iodine in alcoholic solution.

The iodine first disappeared very rapidly, then with more difficulty, and finally the solution took a water-green colour, which was persistent in the cold, and even on heating, or on the addition of hydrochloric acid. Nitric and sulphuric acids both destroy or change it. This reaction is absolutely characteristic of phenol, ($\text{C}_6\text{H}_5\text{OH}$), under the conditions just described.

If we take the phenols most in use, and we consider the diverse reactions produced by the addition of the three substances, alcohol, ammonia, and iodine, in alcoholic solution, we arrive at the following result:—

Different phenols in alcoholic solution:—

Those remaining colourless are—the solutions of phenol (creosote from the beech-tree), thymol, resorcin, naphthol, pyrocatechin, hydroquinone, pyrogallol.

If to these different solutions we add a few drops of pure ammonia, those remaining colourless are—the solutions of phenol (creosote from the beech-tree), thymol, resorcin, and naphthol; those becoming coloured are—the solutions of pyrocatechin, a reddish-brown; hydroquinone, a saffron yellow; pyrogallol, a blackish-brown; orcin, a purple-red, becoming violet.

On the addition of iodine in alcoholic solution to complete absorption, those becoming coloured, though colourless before, are—the solutions of phenol, the characteristic water-green; creosote from beech-trees, a greenish-brown; thymol, flesh coloured, becoming brick-red on the addition of iodine in excess; resorcin, colour of old cognac; naphthol, citron yellow, with the formation of a precipitate of the same colour on the addition of an excess of iodine.

As for the solutions already coloured by the addition of ammonia, on adding iodine that of pyrocatechin becomes cashoo colour without precipitate; that of pyrogallol becomes completely black; that of hydroquinone, saffron-yellow, passing to dark red; that of orcin remains violet.

Gaiacol behaves with this reagent like creosote from the beech, and salicylic acid, which has some analogy with phenic acid with regard to certain reagents, gives a

yellowish-green colour, becoming brown with the formation of a precipitate.

This water-green colour is thus quite characteristic of phenol (C_6H_5OH), and has enabled us to test the purity of white creosotes from coal-tar, sold by druggists and much used by dentists at the present time.

Of four different samples we procured, two consisted of pure phenic acid in solution without traces of *creyol*; the other two contained this latter product, and, in fact, in this case the water-green colour became yellowish-green, and is easily detected by comparison.

This reaction further enables us to detect phenic acid in phenic water at 1, 2, or 3 per cent. It suffices to put x drops in a tube with x drops of alcohol, add the ammonia, then the iodine until the mixture becomes green.

In creosote from the beech, the greenish-brown colour observed tends to become more green, as the creosote is richer in phenol (C_6H_5OH).

Finally, this reaction is only distinct when we use the reagents in the order we have just described. In the presence of soda or potash we never obtained the water-green colour, but a yellowish tint with the formation of a precipitate, which precipitate is also formed under similar circumstances with the other mono- and di-valent phenols, and thus destroys the sharpness of the reaction to be observed.

It is equally indispensable to operate in alcoholic solution; for in aqueous solution, either with exclusively aqueous solutions of phenic acid or by using iodine water, we obtain precipitates which prevent the reaction, and the decompositions which take place in this case are of quite another nature and so well known that they need not be referred to further.—*Bull. des Trav. Pharm. de Bordeaux*, 1901, p. 117.

THE MECHANISM OF THE ACTION OF PEROXIDE OF HYDROGEN ON PERMANGANIC ACID.

By A. BACH.

To explain the mechanism of the action of peroxide of hydrogen on permanganate of potash in acid solution, two hypotheses have been put forward; that of M. Traube, according to which the reduction of the permanganic acid by the peroxide of hydrogen would be due to the oxidisability of the hydrogen of the latter, and that of M. Berthelot, who endeavours to explain the simultaneous reduction of the peroxide of hydrogen and the permanganic acid by the formation of a trioxide of hydrogen, unstable at the ordinary temperature. While the first hypothesis rests on no experimental basis, the second is founded on the well-known experiment in which M. Berthelot has shown that peroxide of hydrogen decolorises permanganate of potash at a temperature of 12° , without giving rise to any appreciable evolution of oxygen. Up to quite recent times, this experiment was generally considered to be quite conclusive, so that Traube's hypothesis had but few upholders.

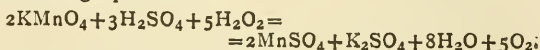
Messrs. Baeyer and Villiger (*Berichte*, vol. xxxiii., p. 2488) have recently repeated M. Berthelot's experiment, and found that the decrease in the evolution of oxygen was due, not to the formation of a trioxide of hydrogen stable at a low temperature, but simply to a phenomenon of supersaturation. Consequently, they consider M. Berthelot's hypothesis to be untenable, and revert to that of M. Traube, saying:—"In the present state of our knowledge we regard this manner of viewing the question (that of Traube) as agreeing best with the known facts, and we are of opinion that the authors of elementary text-books would be quite right in adopting it."

In face of this categorical affirmation, I venture to publish a few observations which help to show that, of the two hypotheses in question, it is not that of M. Traube which agrees best with the facts.

I have attempted to approach the question from the experimental side, and that under the following conditions:—

The excellent work recently published by Messrs. Baeyer and Villiger has shown the existence of a series of derivatives of peroxide of hydrogen, of which one—the hydroethylic peroxide, $H.O.O.C_2H_5$ —seems to be able to furnish the means of verifying Traube's hypothesis by direct experiment.

We know that peroxide of hydrogen reacts on permanganate of potash in acid solution according to the following equation:—



It is evident that this equation agrees as well with M. Traube's hypothesis as with that of M. Berthelot. But the opposite is the case when we use, instead of peroxide of hydrogen, a mono-substituted peroxide of hydrogen which, like hydroethylic peroxide, $H.O.O.C_2H_5$, contains a radical which is almost if not quite unoxidisable. If Traube's hypothesis is really the correct one, that is to say, if the action of the peroxide of hydrogen on permanganate of potash depends on the oxidation of the hydrogen of the peroxide, then hydroethylic peroxide, which does not contain a single oxidisable atom of hydrogen, should require for titration half as much again permanganate as a solution of peroxide of hydrogen containing the same amount of active oxygen. Consequently, when we determine the active oxygen, in accurately weighed quantities of hydroethylic peroxide, first iodometrically, and then by titration by means of permanganate of potash, this latter operation should show—if Traube's hypothesis is correct—half as much again active oxygen as by the iodometric determination. Naturally it is still necessary to take count of the eventual oxidation of the ethyl group in the hydroethylic peroxide, and to subtract from the amount of permanganate used in the titration the amount corresponding to the oxidation of the ethyl or the products derived from it.

The experiments I undertook with hydroethylic peroxide prepared and purified according to Messrs. Baeyer and Villiger's instructions (*Berichte*, vol. xxxiv., p. 738), and taking every possible precaution, gave almost the same values for the iodometric estimation of the active oxygen and for the titration by means of permanganate of potash.

These experiments thus appear to completely disprove Traube's hypothesis, and afford fresh grounds for upholding that of Berthelot.

But a further study of the reaction has shown that the results obtained cannot be used against the hypothesis of Traube or in favour of that of Berthelot, and for the following reason:—

When we titrate a solution of hydroethylic peroxide by means of a solution of permanganate of potash, we observe that the reaction between these two substances only proceeds, even from the commencement, with extreme slowness. It is only after the lapse of one or two hours that the reduction of the permanganate becomes more active to finally pass through the same stages as in the case of peroxide of hydrogen. It was quite possible to imagine that the sulphate of manganese formed played an important rôle in accelerating the reduction of the permanganate by the hydroethylic peroxide. In fact, by adding a certain quantity of sulphate of manganese to the latter, at the commencement of the titration, I found that the progress of the reaction was in every way identical with that which takes place between non-substituted peroxide of hydrogen and permanganate of potash.

It was very probable that, in the presence of sulphate of manganese, the hydroethylic peroxide underwent a hydrolysis, being transformed into peroxide of hydrogen and ethylic alcohol, which would sufficiently explain the fact that the iodometric estimation and the titration of the active oxygen by permanganate of potash gave approximately similar values. The experiments with hydro-

ethylic peroxide did not, therefore, lead to the end I was endeavouring to attain.

I found a better point of comparison in the observation I had occasion to make previously (*Moniteur Scientifique*, 1901, p. 25; *Berichte*, 1900, p. 3111; 1901, p. 1520); that is that the product of the action of concentrated sulphuric acid, or even anhydrous sulphuric acid on dry persulphate of potash, reduced permanganic anhydride, also dissolved in sulphuric acid, concentrated or anhydrous, with great energy, at the same time liberating oxygen.

This product contains a mono-substituted peroxide of hydrogen—mono-persulphuric acid, $\text{HO}_3\text{S.O.OH}$ —which reduces permanganic anhydride under conditions which exclude all possibility of hydrolysis or transformation into peroxide of hydrogen. According to Traube's hypothesis, this product ought to require for titration half as much again permanganic anhydride as a solution of peroxide of hydrogen containing the same quantity of active oxygen.

The experiments previously referred to (*loc. cit.*) were carried out in the following manner:—0.4 gm. of persulphate of potash containing 0.02214 gm. of active oxygen was treated with anhydrous sulphuric acid, the solution was titrated by means of a solution of permanganic acid in anhydrous sulphuric acid, and the oxygen given off was collected over mercury. A solution of peroxide containing the same quantity of active oxygen would have required 8.3 c.c. of permanganic anhydride solution (1 c.c. = 0.002645 gm.), and would set 30.8 c.c. of oxygen at liberty after titration.

Admitting, as is required by Traube's hypothesis, that the atom of hydrogen of the mono-substituted peroxide of hydrogen is oxidised by the permanganic anhydride, we ought to have used 4.15 c.c. of the permanganic anhydride solution for the titration, instead of 8.3 c.c., and equally obtain 30.8 c.c. of oxygen, since, according to Traube, the oxygen set free during the titration comes exclusively from the group —O—O— of the peroxide, of which the hydrogen is oxidised. As a matter of fact, I used 5 c.c. of permanganic anhydride solution for the titration of the product, and collected 24.25 c.c. of oxygen (reduced to 0° and 760 m.m.).

The product, therefore, required more permanganic anhydride, and gave less oxygen than was expected according to Traube's hypothesis.

This deficit of oxygen (6.55 c.c.) shows plainly that the oxygen liberated by the action of the peroxide of hydrogen by the permanganate of potash does not come exclusively from the group —O—O— of the peroxide, for the quantity of oxygen given off should have been independent of the amount of permanganic anhydride used, and have reached about 30.8 c.c.

As we have seen, the product has required 5 c.c. of permanganic anhydride instead of 8.3 c.c.; that is to say, 3.3 c.c. less than a solution of peroxide of hydrogen containing the same quantity of active oxygen. If, now, we compare the amount of disposable oxygen contained in these unused 3.3 c.c. of permanganic anhydride (0.008728 gm. = 6.05 c.c. O), and the above mentioned deficit of oxygen (6.55 c.c.), we see that the two values agree almost exactly. *The deficit of oxygen is the correlative of the diminution of the quantity of permanganic anhydride used in the titration.**

Contrary to Traube's hypothesis, the oxygen set free by the action of the peroxide of hydrogen on the permanganic acid, there seems to be provided, in equal parts, by the two bodies, each atom of active oxygen of the peroxide uniting with an atom of disposable oxygen of the permanganic acid to form a molecule of oxygen, probably with the intermediate production of trioxide of hydrogen.

If we consider that in the titration of the product analysed, more permanganic anhydride was used than was necessary for the oxidation of an atom of hydrogen, we are obliged to admit that the only case in which Traube's hypothesis has been put to experimental proof, is decidedly unfavourable to this hypothesis.

On reviewing all the facts relative to the action of peroxide of hydrogen on permanganic acid, we are bound to arrive at the conclusion that Berthelot's hypothesis is much more plausible and rational than that put forward by Traube. Even admitting that the existence of trioxide of hydrogen is not proved by M. Berthelot's experiment, it nevertheless does not follow that his hypothesis is a false one. We know of a number of reactions in which there is a formation of intermediary products, which up to the present have not been isolated. As in every other respect M. Berthelot's hypothesis seems to be free from objection—this certainly cannot be said of Traube's*—it is not easy to see why the latter should be preferred to the former. In any case, neither of these two hypotheses is yet fit to be included in elementary text-books.—*Moniteur Scientifique*, Series 4, vol. xvi., January, 1902.

CHEMICAL SOCIETIES OF THE NINETEENTH CENTURY.†

By HENRY CARRINGTON BOLTON, Ph.D.

THE beginning of a new century affords an opportune period for chronicling the progress of chemistry as shown by the organisations formed to foster its study and to stimulate its adherents. In the following pages an attempt has been made to place on record the statistics of the Chemical Societies of the World for the year 1900, and to indicate those that ended their careers within the nineteenth century. The data have been obtained chiefly by correspondence, and thanks are due to the officers of societies who have responded to inquiries. I am also under special obligations to Dr. Paul Dorveaux, Librarian of the Ecole Supérieure de Pharmacie, Paris; to Professor Bohuslav Brauner, of the Bohemian University, Prague; to Professor George W. A. Kahlbaum, of the University of Basel; and particularly to the Smithsonian Institution, for aid in securing the information sought.

The fact that chemical societies were organised and in operation in the United States of America long before they existed in Europe has been shown in my paper, "Early American Chemical Societies," read to the Chemical Society of Washington, April 8, 1897. The two pioneers in this field were the Chemical Society of Philadelphia, founded in 1792, and the Columbian Chemical Society of Philadelphia, founded in 1811. Of these, some particulars will be found in their proper order.

In the following list the societies are placed in chronological order under each country, and the countries are arranged alphabetically. Of each society the following data are given so far as attainable:—

Seat, and date of founding.

Name of President, and membership in 1900. (No deductions have been made for duplication).

Serial publications. (For full details consult "A Select Bibliography of Chemistry," by Henry Carrington Bolton, Washington, 1893-1899, 3 vols., 8vo).

Remarks.

The results of this census are given in the following table:—

* The cause of this diminution is probably due to the formation of a superoxygenated peracid—a derivative of tetroxide of hydrogen—the consequence of which is to render inactive a portion of the active oxygen, since the atoms of this latter unite in groups of three to form compounds containing, like ozone, a chain of three atoms of oxygen, of which only one is active.

* To admit, as is done by Traube, that peroxide of hydrogen contains easily oxidisable hydrogen, united directly with active oxygen, seems contrary to reason.

† Read at the Twenty-fifth Anniversary of the American Chemical Society, held in New York City, April 12-13, 1901. From advance proofs of the *Smithsonian Miscellaneous Collections*, 1901.

CHEMICAL SOCIETIES OF THE WORLD.

Membership in 1900.

Country.	No. of societies.	No. of members.
Austria	7	3072
Belgium	3	740
France	10	4065
Germany	10	7559
Great Britain	9	7550
Italy	5	479
Japan	2	1012
Russia	1	327
South Africa	1	(?)
Switzerland	2	94
United States America	5	2379
Victoria	1	100
Totals	56	27,377

AUSTRIA.

CENTRALVEREIN FÜR RÜBENZUCKER INDUSTRIE IN DER OESTERREICHISCH-UNGARISCHEN MONARCHIE.

Founded at Vienna in 1854. In 1900: President, August Freiherr von Stummer; members, 213; associates, 49.

Publications.—Organ des Vereins für R.-I., 1863-1874; Organ des Centralvereins für R.-I., 1875-1887; Oesterreichisch-ungarische Zeitschrift für Zucker-Industrie und Landwirtschaft, 1888-1900. (Beilagen).—Der Marktbericht, 1874-1885; Wochenschrift des Centralvereins für Rüben-zucker in der oesterreichisch-ungarischen Mon-archie, 1886-1900.

NOTE.—The Society maintains a Chemical Experiment Station under the direction of F. Stohmer.

VEREIN ZUR HEBUNG DER ZUCKERFABRIKATION IM KÖNIGREICH BÖHMEN. (Also with a Bohemian name).

Founded at Prag in 1868 under the presidency of Ferdinand Urbánek; the languages used were Bohemian and German. It was disbanded in 1874.

Publication.—Zeitschrift für Zucker-Industrie. Organ des Vereins. Prag. 3 vols., 1872-74.

NOTE.—This journal is not to be confounded with *Zeitschrift für Zucker-Industrie in Böhmen*, established at Prag in 1877 and current.

CHEMICKÁ SPOLEČNOST: SPOLEK ČESKÝCH CHEMIKŮ. (Chemical Society: Union of Bohemian Chemists).

Founded at Prag in 1872. In 1900: President, K. Preis; honorary members, 11; active members, 318; cor-respondents, 77.

Publications.—Zprávy spolku českých chemiků. 2 vols., 1872-76. (Reports). Listy Chemické, 1877-1900. (Letters).

NOTE.—The Society has also published a Chemická Knihovna (Chemical Library) in 8 vols.

ZEMSKÝ SPOLEK PRO PRŮMYSL CUKROVARNICKÝ V ČECHÁCH; VEREIN DER ZUCKERINDUSTRIE IM KÖNIGREICH BÖHMEN.

Founded at Prag in 1876. In 1900: President, Gustav Hodek; members, 325.

Publications.—Zeitschrift für Zucker-Industrie in Böhmen, 1877-1900. (Beilage).—Prager Zucker-markt, 1881-1900.

OESTERREICHISCHE GESELLSCHAFT ZUR FÖRDERUNG DER CHEMISCHEN INDUSTRIE.

Founded in Prag in 1878. In 1900: President, Georg Zetter; honorary members, 3; members, 196.

Publications.—Bericht der oesterreichischen Gesell-schaft zur Förderung der chemischen Industrie, 1879-98. Since 1899 the organ of the Society is Oesterreichische Chemiker-Zeitung.

SPOLEČNOST PRO PRŮMYSL CHEMICKÝ.
(Society of Chemical Industry).

Founded in 1892 at Prag. In 1900: President, J. B. Lambl; honorary members, 20; active members, 440; correspondents, 54; founders, 57.

Publications.—The organ of the Society since 1892 is *Casopis pro průmysl chemický*, of Prag, which had been established in 1891. The Society has also published three volumes of a technological library, *Knihovna technologicko chemická*.

WIENER VEREIN ZUR FÖRDERUNG DES PHYSIKALISCHEN UND CHEMISCHEN UNTERRICHTS.

Founded in 1895 at Vienna. In 1900: President, Victor von Lang; members, 317.

Publication.—Vierteljahrsberichte der Wiener Verein zur Förderung des physikalischen und chem-ischen Unterrichts, 1895-1900.

VEREIN OESTERREICHISCHER CHEMIKER IN WIEN.

Founded in 1897 at Vienna. In 1900: President, J. Klaudy; members, 878; founders, 14.

Publication.—Oesterreichische Chemiker Zeitung, 1898-1900.

BELGIUM.

ASSOCIATION BELGE DES CHIMISTES.

Founded August 4, 1887, at Brussels. In 1900: Presi-dent, L. L. de Koninck; honorary members, 4; active members, 482; associates, 21; correspondents, 8.

Publication.—Bulletin de l'Association Belge des chimistes, 1887-1900.

NOTE.—The Association has eight sections, viz., Liège, Louvain, Gembloux, Charleroi, Mons, Gans, Antwerp, Brussels.

SOCIÉTÉ TECHNIQUE ET CHIMIQUE DE SUCRERIE DE BELGIQUE.

Founded February 26, 1896, at Brussels. In 1900: President, Eugène Meeus; members, 173; patron, 1.

Publications.—La sucrerie Belge, which was estab-lished August 31, 1872, has been the organ of the Society since its foundation. The Society has also published several pamphlets on technical topics.

NOTE.—The formation of Sections was under discussion in 1900.

SYNDICAT DES CHIMISTES PUBLICS DE BELGIQUE.

Founded in 1897 at Brussels. In 1900: President, François Sachs; members, 51.

Publication.—Bulletin du Syndicat des Chimistes publics de Belgique, 1897-1900.

NOTE.—The Society has in preparation "Recueil générale des méthodes d'analyse usitée dans les labora-toires publics."

SOCIÉTÉ GÉNÉRALE DES FABRICANTS DE SUCRE DE BELGIQUE is not a chemical society; its organ is *La sucrerie Belge*, 1872-1900.

(To be continued).

Action of Organo-magnesium Compounds on β -Ketonic Ethers.—V. Grignard.—The author's re-searches on this subject show that, in presence of organo-magnesium compounds, (1) acetylacetic ether reacts only in its enolic form; (2) its monoalcoyl derivatives are really mixtures of the ketonic and enolic forms; (3) the products of condensation of the aldehydes with acetoacetic ether possess Claisen's formula.—*Comptes Rendus*, cxxxiv., No. 15.

A NEW INVESTIGATION CONCERNING THE
ATOMIC WEIGHT OF URANIUM.*By THEODORE WILLIAM RICHARDS
and
BENJAMIN SHORES MERIGOLD.

(Continued from p. 209).

Methods of Analysis.

By the use of these devices we were able to prepare and weigh pure uranous bromide in a definite state. There still remained, however, the problem of devising a suitable method of analysis. As previously mentioned, all uranous compounds reduce silver nitrate, making impossible the usual method of procedure in halogen determinations.

The method of precipitating the uranium and determining bromine in the filtrate involves too much danger of loss of material in the multiplicity of operations. The most satisfactory solution of the problem seemed to be to oxidise the compound to the uranyl salt, provided this could be done without loss of bromine. Nitric acid is of course effective as an oxidising agent, but the oxidation is accompanied by loss of bromine. After much experimenting, hydrogen dioxide was found to be the most suitable oxidiser. From neutral solutions of uranium compounds, hydrogen dioxide precipitates a hydrated peroxide of uranium. If the solution is slightly acid, this precipitation is prevented, and the uranous compound completely oxidised to the uranyl state. The weighed sample of uranous bromide was dissolved in considerable water—at least 400 c.c. of water to each gm. of bromide. The bottle containing the bromide was opened by means of a suitable glass fork, either below the water or just above the surface, so that it could be instantly submerged, and thus avoid loss of hydrobromic acid by the action of moist air. The calculated volume of a standard solution of pure hydrogen dioxide was then diluted to about 100 c.c., 1 c.c. of pure dilute sulphuric acid was added, and the mixture was slowly run into the solution of uranous bromide. The green colour of the uranous salt soon changes to the yellow colour characteristic of uranyl compounds. On adding the first few c.c. of the dilute hydrogen dioxide solution, a greenish-white precipitate came down. Addition of more of the acid dioxide solution re-dissolved it, and the resulting solution was perfectly clear. This peculiar hydrolytic action is due to the acid, and not to the hydric dioxide, for the same reaction occurs if dilute sulphuric acid alone is added to the solution.

The explanation of this interesting phenomenon, which is just the opposite of what might have been expected, is, undoubtedly, that the bromide is already hydrolysed to a great extent by merely dissolving in water. The hydrate is probably in solution in the colloidal state. Evidence of this is found in the fact that if the clear aqueous solution of uranous bromide is allowed to stand exposed to the air, a hydrate gradually separates, giving to the solution a cloudy, murky appearance. After two or three days this precipitate disappears, giving place to a clear yellow solution of oxybromide and hydrobromic acid. The addition of sulphuric acid coagulates the colloid before it can all be converted into uranyl salt.

In order to be sure that no bromine or hydrobromic acid is lost by this method of oxidation, the following experiment was made:—0.5 gm. of bromide was dissolved in 250 c.c. of water, 50 c.c. of dilute sulphuric acid (1:10) was added, and the hydrogen dioxide solution was run in. This was done in a closed flask, similar in construction to a gas washing bottle. A current of air was drawn through the bottle and then through starch solution containing potassium iodide to see if bromine is liberated. Not the slightest trace of blue colour appeared in the starch solution, even after adding a large excess of

hydrogen peroxide, and allowing it to stand over night. A test for hybromic acid was sought in a similar way, by drawing the air through a solution of silver nitrate, again with negative results, as was to have been expected. These experiments show conclusively that uranous bromide can be oxidised completely by hydrogen dioxide, without loss of bromine.

Silver nitrate, in moderately concentrated solutions is not acted upon by a 3 per cent solution of hydrogen peroxide. Consequently, a considerable excess of the latter reagent could do no harm. Nevertheless, care was taken never to add more than the calculated amount of hydrogen dioxide. Moreover, the solution of hydrogen dioxide used contained only 1 per cent of this reagent, and this was diluted ten times before adding to the bromide solution, thus reducing to a minimum the possibility of too vigorous oxidation, with consequent liberation of bromine.

After the oxidation, bromine was precipitated by pure silver nitrate in the usual manner. This precipitation was conducted in an Erlenmeyer flask fitted with a glass ground stopper. The silver bromide was collected on a Gooch crucible, and dried in an electrically heated drying oven. Of course the asbestos shreds carried away in washing the silver bromide were collected by passing the filtrate and wash water through a fine filter, and their weight was added to that of the silver bromide. The bromine determination was carried on in orange-coloured light.

It was found in the work upon cobalt and nickel that the porcelain tube is attacked by bromine vapour at the high temperature employed during the sublimation, with the result that sodium bromide was always present in the sublimate. In these investigations this impurity was determined by the reduction of the bromide to the spongy metallic state by means of hydrogen and extraction by water (*Proc. Amer. Acad. Arts Sci.*, 1899, xxxiv., 329, 359). A somewhat similar method was tried with uranium. Since hydrogen reduces uranous bromide only to the tri-bromide, the bromide was ignited in a current of air, and the resulting oxide leached with water. It was found to be impossible to oxidise the bromide completely. A little uranous bromide invariably remained, and was washed out with the alkali. Both dry and moist air was tried, also ignition in steam, but in every case uranium was washed out in considerable quantity.

Precipitation of the uranium by hydrogen dioxide was next tried, but it was found impossible to precipitate the uranium completely. The rather unsatisfactory method of determining the sodium in the filtrate from the bromine precipitation, or in a new sample of uranous bromide as nearly as possible, after removing the uranium with ammonium sulphide, appeared to be the only available method. The filtrate and wash waters from the bromine precipitation were evaporated in platinum to small bulk, and the uranium and excess of silver precipitated by pure colourless ammonium sulphide. This reagent precipitates uranium completely. The filtrate was then evaporated to dryness, the ammonium salts expelled by ignition, and the residual sodic nitrate converted to the sulphate, and weighed as such. Of course these operations were all conducted in platinum vessels. This method of work is not wholly satisfactory, on account of the complexity of operations involved, but it seems to be the only practical method.

Purification of Materials.

As the source of uranium, commercial "chemically pure" uranium acetate was used.* This was first converted to the chloride on account of the greater solubility of this compound—by precipitation as ammonium uranate, and re-dissolving in dilute hydrochloric acid. To the hot and slightly acid solution, pure sulphuretted hydrogen was added to saturation. The free acid was then neutralised

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxvii., No. 14.

* This method of uranium purification, with some modifications and additions, is similar to that employed by Zimmermann (*Ann. der Chem. u. Pharm.*, ccxxxii., 299).

with ammoniac hydroxide, a slight excess of the alkali was added, and more sulphuretted hydrogen was run in. In this way some uranyl sulphide was precipitated, in order to sweep down with it any colloidal sulphides of the higher groups which might otherwise escape removal. The excess of sulphuretted hydrogen was boiled off, and after standing over night the supernatant liquid was decanted through a washed filter.

The next step depended upon the fact that uranium remains in a solution of the double carbonate of ammonium and uranium, in the presence of an excess of ammonium sulphide, while all the other members of the aluminum and iron groups are thrown down by this reagent. Consequently, ammoniac hydrate and ammonium carbonate in slight excess were added to the filtrate, forming the double carbonate. If the solutions are concentrated, the double carbonate is precipitated when more than a slight excess of ammoniac carbonate is used. This happened in some cases, when it was necessary to re-dissolve the precipitate in dilute hydrochloric acid, and again add ammoniac carbonate in more dilute solution. About 50 grms. of carbonate per litre was found to give the best results. Ammoniac hydroxide was then added to the hot solution, and sulphuretted hydrogen in excess. After standing over night the solution was filtered. In several of the more concentrated solutions, a considerable quantity of the salt crystallised out. These crystals were worked up separately, as they were probably purer than the solution. On boiling the solution to decompose the excess of ammonium sulphide, some of the ammoniac carbonate was decomposed, causing the precipitation of some uranium sulphide. This precipitate was discarded, as it might have contained iron, or other analogous metals which had previously escaped precipitation. Dilute hydrochloric acid in slight excess was added, and the carbon dioxide was expelled by boiling. The free acid was then almost neutralised with pure ammoniac hydroxide, and pure ammoniac sulphhydrate added in excess. The colour of the resulting precipitate of uranium sulphide varies greatly with the temperature. In warm solution it was at first reddish-brown, while that precipitated in the cold varied from bright red to brownish-yellow. On washing, all turn black, the sulphide being decomposed into uranous oxide and sulphur. After thorough washing the resulting mixture of oxide and sulphur was ignited in a porcelain dish, the green urano-uranic oxide being the product.

The oxide was then dissolved in a platinum dish in re-distilled nitric acid, evaporated and re-crystallised from nitric acid solution. Uranyl nitrate does not crystallise well from aqueous solution, but it was found that if a little nitric acid is added, it crystallises readily in fairly large monoclinic prisms. This re-crystallisation was repeated ten times from acid solution, and, finally, twice from aqueous solution. Finally, the pure nitrate was converted to the oxide by ignition in platinum. A second sample, used in the preliminary series, was prepared by repeated fractionation of the mother-liquors of the first sample.

Since this work was carried out, Sir William Crookes (*Proc. Roy. Soc.*, 1900, lxvi., 409) has published the account of several methods by which he was able to prepare specimens of uranyl nitrate which were not radio-active. The radio-activity of uranium has hitherto been supposed to be characteristic of this element. Crookes has shown, however, that this is not the case, but that the active element can be separated by treatment with ether, by fractional crystallisation, or by treatment with excess of ammonium carbonate. Unfortunately, none of the pure oxide prepared for this investigation remained, hence it is impossible to test directly its radio-activity. Since two of Crookes's method were used in purifying our material, viz., the ammonium carbonate treatment and fractional crystallisation, it is highly improbable that our oxide was radio-active. In repeating Crookes's work with nitrate made from some of the same material used in preparing our best nitrate, it was found that a sample of the *fifth* crystallisation gave no trace of action on twenty-four hours'

exposure to a quick photographic plate. The material used in this experiment had not been submitted to the ammonium carbonate treatment. When it is considered that the material used for our atomic weight determinations was first put through the carbonate process—in itself sufficient to remove the radio-active element—and then was re-crystallised *twelve times* as nitrate, it would seem that our pure oxide must have been free from all radio-active material.

There is another phase of this subject that deserves to be considered, namely, the possible effect of radio-active matter, even if present, upon the atomic weight value. The purest specimen of radium or "polonium" yet obtained has consisted of a mixture containing probably little more than 50 per cent of the active element, as nearly as could be estimated. This highly impure material, however, possesses 8000 times the radio-activity of uranium. The radio-active power of the pure material is undoubtedly very much greater than that of the impure mixture. Consequently, the quantity of radio-active substance necessary to give to uranium the comparatively slight degree of activity that it possesses must be exceedingly minute. Giesel has recently shown (*Berichte*, 1900, xxxiii., 3569) that a quantity of radium so small that it cannot be detected by sulphuric acid is sufficient to affect a photographic plate. Crookes also says on this point:—"Considering my most active UxX does not contain sufficient of the real material to show in the spectrograph, yet is powerful enough to give a good impression on a photographic plate in five minutes, what must be its dilution in compounds which require an hour, a day, or a week to give an action?" (*Proc. Roy. Soc.*, 1900, lxvi., 422). Even in the ordinary active uranium compounds it is most unlikely that the active element—if indeed it is an element—could possibly be present in quantity sufficient to exert any influence whatever upon the atomic weight of uranium.

Pure carbon was obtained by ignition of sugar. Large, clear crystals of the best "rock candy" of commerce were ground up in a porcelain mortar, and ignited at low heat in a platinum dish as long as organic gases were given off. The resulting charcoal was then powdered in an agate mortar, and ignited in a hard glass combustion tube; first in a stream of pure, dry nitrogen, and finally in a stream of bromine vapour. In this way the carbon was freed from any impurities which might, if present, be acted upon during the sublimation, and contaminate the sublimate. Owing to the presence of undecomposed carbohydrates, or possibly of water, most of the bromine was converted into hydrobromic acid. Heating in bromine was continued until acid fumes ceased to be given off. Finally, the carbon was again heated in a current of dry nitrogen. Five grms. of carbon, thus prepared, left no visible or weighable residue after combustion in oxygen.

The method of bromine purification was essentially identical with that used in many other atomic weight investigations in this laboratory, and has been proved by long experience to be the most efficient and satisfactory. Commercial, "pure" bromine was partially freed from chlorine by shaking with a 15 per cent solution of potassium bromide. One-fourth of the bromine was then converted to calcic bromide by running it slowly into milk of lime in the presence of a large excess of ammonia. The calcic bromide solution was filtered and concentrated by evaporation, and the rest of the bromine was added to it. A little zinc oxide was then added, and after standing over night the bromine was distilled, nearly free from chlorine. Most of the iodine is removed as zinc iodate. After re-distilling the bromine, in order to remove any calcium bromide that may have spattered over in the first distillation, it was converted into hydrobromic acid by slowly dropping it into a mixture of red phosphorus and hydrobromic acid. The red phosphorus was at first washed free from chlorides. The hydrobromic acid, containing some free bromine, was distilled. The free bromine liberates any iodine which may have escaped the zinc oxide. The first portion of

the distillate, containing free bromine and iodine, and organic matter, was rejected, and so was the last portion, which may have contained traces of arsenic. The hydrobromic acid was then converted into bromine by distilling over pure manganese dioxide previously treated with sulphuric acid and washed. One-half the bromine is obtained by the manganese dioxide alone. As soon as no more bromine comes off, a little re-distilled sulphuric acid is added, and the rest of the bromine was obtained. It was then re-distilled several times, rejecting the first and last portions, and finally dried over pure phosphorous pentoxide.

The silver precipitation also presents no new features, except, perhaps, its somewhat unusual thoroughness. Partially purified silver was dissolved in nitric acid, diluted, and precipitated with pure hydrochloric acid. After thorough washing the chloride was reduced by invert sugar and sodic hydrate which had been purified by electrolysis. The metallic silver was thoroughly washed, dissolved in nitric acid, and again precipitated as chloride, and reduced. It was then dried and fused on charcoal; the lumps of silver were cleaned with sand, dissolved in pure nitric acid, diluted to a volume of two litres, and again precipitated with pure hydrochloric acid. The resulting chloride was then digested on the steam bath with aqua regia, washed, and once more reduced by invert sugar and sodic hydrate. After drying, it was fused on pure sugar charcoal. The buttons of silver were cleaned with sand, and then purified electrolytically, a small portion being dissolved in nitric acid to serve as the electrolyte, and the rest serving as anode material. The crystals of electrolytic silver were then dried over potash, and fused *in vacuo* on a boat of pure lime. The buttons of silver thus obtained were treated with nitric acid to remove the surface, dried, and kept over potash. A second sample was obtained by fusing *in vacuo* electrolytic silver which had been prepared from the silver bromide obtained in Dr. Baxter's work upon cobalt, which was known to be very pure.

Hydric dioxide was purified as follows.—To a solution of the ordinary commercial peroxide prepared for medicinal use, was added a solution of baric hydroxide, which had been purified by re-crystallisation. The precipitated baric dioxide was washed until a nitric acid solution of the same showed no trace of halogen. It was then added to pure dilute sulphuric acid, and the resulting solution of hydric dioxide was filtered and distilled in a partial vacuum. The solution thus obtained showed no trace of halogen, and left no visible residue on evaporation in platinum.

Ammonium sulphide was made from pure ammonia, which had been re-distilled in platinum, and pure sulphuretted hydrogen. It left no visible residue on evaporation in platinum.

Hydrochloric and nitric acids were re-distilled in a platinum still, and throughout the work platinum vessels were used wherever possible.

Water was twice re-distilled, once over alkaline potassic permanganate, and again over acid potassic sulphate from a Jena glass flask, a block-tin condenser and Jena glass receiver being used.

(To be continued).

The Mutual Reaction of Arsenious Acid and Permanganate.—O. Kühling.—The estimation of arsenious acid can be effected in a very satisfactory manner by means of a titrated solution of permanganate, proceeding in the same way as for phosphorous acid (*Berichte*, vol. xxxiii., p. 2914). As in this latter case, we can use sulphate of zinc to facilitate the oxidising action of the permanganate, but it is still more simple to use a 10 to 20 per cent solution of sulphuric acid. The operation should be carried out in a nearly boiling solution, and it is best to add almost the whole of the permanganate necessary for the oxidation at one time.—*Berichte*, vol. xxxiv., p. 404.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, April 17th, 1902.

Prof. TILDEN, D.Sc., F.R.S., Treasurer, in the Chair.

MESSRS. Davis, Dorée, Aders Plimmer, Allworthy, and Bedwell were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Thomas Clough, 3, Watford Villas, Battersea Park, S.W.; Henry Wilson Davis, 18, Crescent Road, Kingston Hill, Surrey; Thomas Butterworth Hallowell, New Mills, Derbyshire; Charles B. Lessner, 46, Broadfield Road, Hither Green, S.E.; Thomas Henry Moore, 19, Sandmere Road, Clapham, S.W.; Prafulla Chandra Ray, Calcutta, India; William Pearson Skerchly, 11, Billiter Square, E.C.; Hector Stewart, 479, Collins Street, Melbourne; William John Wells, Springburn, Blackburn; Joseph West, 50, Poplar Grove, Fenton, Stoke on-Trent.

Of the following papers, those marked * were read:—

*56. "*Dimercurammonium Nitrite and its Haloid Derivatives.*" By P. C. RAY.

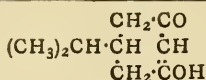
Some account has already been given (*Proc.*, 1901, xvii., 96) of the investigation which is here more fully and accurately described. Mercurous nitrite partly decomposes in dissolving in water, giving metallic mercury and a solution of both mercuric and mercurous nitrites (*Trans.*, 1897, lxxi., 337). Adding to this solution just enough sodium chloride and filtering, there is left a solution of mercuric sodium nitrite, which gives, with excess of ammonia, a white precipitate of a new salt, $2\text{NHg}_2\text{NO}_2\cdot\text{H}_2\text{O}$, dimercurammonium nitrite. On dissolving it in hydrochloric acid and evaporating, there is left a new mercuric ammonium chloride, $2\text{HgCl}_2\cdot\text{NH}_4\text{Cl}$, a white, crystalline, volatile, and fusible salt. The corresponding bromide can be obtained in a similar way, as well as by evaporating a hydrobromic acid solution of the single bromides in the right proportions; it is largely decomposed by water into its component salts. With potassium hydroxide, not in excess, these double salts give dimercurammonium chloride and bromide, $2\text{NHg}_2\text{Cl}\cdot\text{HgCl}_2$ and $2\text{NHg}_2\text{Br}\cdot\text{HgBr}_2$, the former not quite pure. With excess of potassium hydroxide, they yield the half-hydrated dimercurammonium chloride and bromide, $2\text{NHg}_2\text{Cl}\cdot\text{H}_2\text{O}$ and $2\text{NHg}_2\text{Br}\cdot\text{H}_2\text{O}$, the former already described by André.

When either dimercurammonium chloride or bromide is dissolved in hydrobromic acid, the above formulated mercuric ammonium bromide is obtained on evaporation; when dimercurammonium bromide is dissolved in hydrochloric acid, a mercuric ammonium chlorobromide, $2\text{HgCl}_2\cdot\text{NH}_4\text{Br}$, is left on evaporation. From this chlorobromide, potassium hydroxide reproduces quantitatively dimercurammonium bromide, a fact which led the author at first to regard the chlorobromide as dimercurammonium bromide in union with 4 molecules of hydrochloric acid, and the corresponding double chloride and double bromide as $\text{NHg}_2\text{Cl}_4\cdot\text{HCl}$, and $\text{NHg}_2\text{Br}_4\cdot\text{HBr}$, respectively.

The author considers that the chemical composition of dimercurammonium nitrite and its derivatives gives much support to the Rammelsberg-Pesci theory of the dimercurammonium constitution of all ammoniated mercury salts.

*57. "*Preparation and Properties of 4-isopropylidihydroresorcin.*" A Correction. By A. W. CROSSLEY.

The nomenclature adopted in the preliminary notice of this work (*Proc.*, 1901, xvii., 172) has been changed. The substance there spoken of as 2:6-diketone-4-isopropylhexamethylene is now called 4-isopropylidihydroresorcin, for though this and other similar substituted dihydroresorcins behave as diketones towards hydroxylamine, there can be no doubt that their most usual form is the keto-enol modification represented by the following formula:—



*58. "Oxonium Salts of Fluoran and its Derivatives." By J. T. HEWITT and J. N. TERVET.

Fluoran (the phenolphthalein anhydride of Baeyer) and some of its derivatives have been examined as to their power of forming salts with strong mineral acids. The following salts have been prepared and examined:—*Fluoran nitrate*, $\text{C}_{20}\text{H}_{12}\text{O}_3, \text{HNO}_3$; *monosulphate*, $\text{C}_{20}\text{H}_{12}\text{O}_3, \text{H}_2\text{SO}_4$; *dimethylfluoran nitrate*, $\text{C}_{22}\text{H}_{16}\text{O}_3, \text{HNO}_3$; *dimethylfluoran monosulphate*, $\text{C}_{22}\text{H}_{16}\text{O}_3, \text{H}_2\text{SO}_4$; *dimethylfluoran disulphate*, $\text{C}_{22}\text{H}_{16}\text{O}_3, 2\text{H}_2\text{SO}_4$; *fluorescein hydrochloride*, $\text{C}_{20}\text{H}_{12}\text{O}_5, \text{HCl}$; *fluorescein monosulphate*, $\text{C}_{20}\text{H}_{12}\text{O}_5, \text{H}_2\text{SO}_4$; *fluorescein disulphate*, $\text{C}_{20}\text{H}_{12}\text{O}_5, 2\text{H}_2\text{SO}_4$.

*59. "Influence of Substitution on the Reactivity of the Aromatic Metadiamines." By G. T. MORGAN, D.Sc.

The successive introduction of methyl groups into the three positions adjacent to the nitrogen atoms of *m*-phenylenediamine is attended by a well-marked diminution in the reactivity of the diamine towards methylating agents, the action of methyl chloride or bromide being prevented when the substitution of the three hydrogen atoms is complete.

m-Tolylenediamine (2 : 4-diaminotoluene), like *m*-phenylenediamine, gives rise to a mixture of tertiary base and quaternary salt; 4 : 6-diamino-*m*-xylene yields the tertiary base as the sole product, whilst diaminomesitylene is not affected.

These results agree with those obtained by Pinnow (*Ber.*, 1897, xxx., 3110; 1899, xxxii., 1401; 1901, xxxiv., 1129), and also by E. Fischer and Windaus (*Ber.*, 1900, xxxiii., 345 and 1967).

The tertiary diamines containing one free para-ortho-position with respect to nitrogen are very reactive substances, darkening on exposure, yielding unstable platinum chlorides, and interacting readily with formaldehyde and the diazonium salts.

4 : 6-Tetramethyldiamino-*m*-xylene, which contains methyl groups in each of the para-ortho-positions, is a comparatively inert substance which is not darkened by exposure to light or air; its *platinichloride* is stable, and the base itself does not condense either with formaldehyde or diazonium salts. This diamine boils at 243–245° under 757 m.m., and at 124–125° under 12 m.m. pressure; its *picrate* crystallises in yellow prisms melting when suddenly heated at 202–203°, but decomposing at 193–195° when maintained at this temperature for some time.

2 : 4-Tetramethyldiaminotoluene is a pale brownish-yellow oil boiling at 254–256° under 757 m.m., and at 148–150° under 24–26 m.m. pressure; its sp. gr. is 0.9661 at 24°; its *platinichloride* is decomposed by hot water; the *picrate* crystallises from alcohol in yellow prisms melting at 162–163°. The *methobromide*, $\text{NMe}_2\cdot\text{C}_6\text{H}_3(\text{CH}_3)\text{NMe}_3\cdot\text{Br}$, produced together with the tertiary diamine in the methylation of *m*-tolylenediamine, yields a *platinichloride*, $\text{NMe}_2\cdot\text{C}_6\text{H}_3(\text{CH}_3)\text{NMe}_3\cdot\text{HPtCl}_6$, crystallising in brownish-yellow scales.

p-Nitrobenzene-5-azo-2 : 4-tetramethyldiaminotoluene, resulting from the action of *p*-nitrobenzenediazonium chloride on 2 : 4-tetramethyldiaminotoluene, crystallises from alcohol or ethyl acetate in dark green leaflets with a bronze reflex, and melts at 126–127°.

2 : 4 : 2' : 4'-Octamethyltetraminoditolyl-5 : 5'-methane, prepared by condensing 2 : 4-tetramethyldiaminotoluene with formaldehyde, crystallises from alcohol in colourless prisms melting at 86°; its *picrate* separates in spherical aggregates of yellow crystals, and melts at 147–148°.

60. "The Influence of certain Acidic Oxides on the Specific Rotations of Lactic Acid and Potassium Lactate." By G. G. HENDERSON and D. PRENTICE, Ph.D.

The authors have examined the influence of antimonious, arsenious, and boric oxides on the rotations of

aqueous solutions of potassium lactate and lactic acid, with the object of ascertaining whether any compounds of the tartar emetic type are formed in solution by interaction of these substances.

It was found that antimonious oxide is almost insoluble in solutions of potassium lactate, and that the rotations of the solutions are not appreciably affected by the presence of traces of antimonious oxide. Arsenious oxide and boric acid, on the other hand, were found to dissolve readily in aqueous solutions of potassium lactate and lactic acid. The rotations of the solutions are altered by the presence of the dissolved oxide, and in each case the maximum change occurs when the substances are present in the proportions requisite for the formation of an arseniolactate, $(\text{AsO})\text{C}_3\text{H}_4\text{O}_3\text{K}$, and a borolactate, $(\text{BO})\text{C}_3\text{H}_4\text{O}_3\text{K}$, respectively. The rotation of a solution of lactic acid is slightly diminished when arsenious oxide is dissolved in it, but considerably increased by the presence of boric acid.

Experiments with molybdc and other oxides are in progress.

61. "The Amounts of Nitrogen as Ammonia and as Nitric Acid, and of Chlorine in the Rain-water Collected at Rothamsted. A Report to the Lawes Trust Committee." By N. H. J. MILLER.

Results of monthly determinations of nitrogen as ammonia and as nitrates in the rain-water collected during thirteen harvest years (September, 1888, to August, 1901) at Rothamsted showed that the total nitrogen in these forms varied from 3.31 lbs. to 4.43 lbs. per acre per annum. The average amounts for the winter and summer months, and for the whole year are as follows:—

	Rainfall (inches).	Nitrogen per million		Nitrogen per acre (lbs.)		Total.
		as ammonia.	as nitrates.	as ammonia.	as nitrates.	
Winter.	14.32	0.381	0.175	1.233	0.568	1.801
Summer	12.93	0.506	0.191	1.479	0.560	2.039
Year ..	27.25	0.440	0.183	2.712	1.128	3.840

Of the total nitrogen 70 per cent is present as ammonia and 30 per cent as nitrates. During the summer months there is an increased production of ammonia, whilst the amount of nitric nitrogen (per acre) is nearly the same in summer as in winter.

Chlorine has been determined monthly for twenty-four years. The average amounts are as follows:—

	Rainfall (inches).	Chlorine	
		per million.	per acre (lbs.).
Sept. 1877 to Aug. 1901.			
Winter months ..	14.65	3.05	10.12
Summer months ..	14.13	1.49	4.75
Year	28.78	2.28	14.87

The yearly amounts of chlorine in the rain vary considerably (maximum 21.19, minimum 10.32 lbs. per acre). The variations depend less on the total rainfall for the year than on the amount of rain during the winter months.

The rain falling at Rothamsted supplies, not only sufficient chlorine, but also enough sulphuric acid for the requirements of most crops.

62. "The Amounts of Nitrogen, as Nitrates, and Chlorine in the Drainage through Uncropped and Unmanured Land. A Report to the Lawes Trust Committee." By N. H. J. MILLER.

The percolation through the 20, 40, and 60 inches of soil in the three Barnfield drain gauges amounted during 24 harvest years, Sept. 1877 to Aug. 1901, to 14.39, 15.30, and 14.41 inches per annum, being 50.0, 53.2, and 50.1 per cent respectively of the rainfall for the same period. The maximum and minimum drainage occur in November and June.

The average loss of nitrogen, as nitrates, in the drainage is more than 30 lbs. per acre per annum, and about half of this loss takes place during October, November, and December. The yearly losses of nitrogen differ widely, according to the amount and distribution of the rain and drainage. This makes it difficult to form a decided opinion as to whether nitrification is less active at

the present time than in earlier years. A very decided falling off is perhaps not to be expected in the near future. The soil of the 20-inch gauge is estimated to have contained, in 1870, as much as 6000 lbs. of nitrogen per acre, and of this amount only about 15 per cent has been found in the drainage; in the case of the 60-inch gauge, the estimated loss is only 6·5 per cent of the total initial nitrogen of the soil. In addition to loss of nitrogen, there is, however, a considerable loss of lime, amounting to 11 lbs. per acre (or about 20 lbs. of calcium carbonate) per inch of drainage, and this loss may, as time goes on, be expected to influence the changes in the organic matter of the soils.

The average yearly amounts of chlorine per acre in the drainage is very similar to the amount found in the rain, but wide differences occur in some individual years. In the twenty four years during which the chlorine has been determined, the soils of the 20-inch and 40-inch gauges have received from the rain 7·0 and 14·4 lbs. of chlorine per acre in excess of the amounts lost in drainage. The 40-inch gauge has lost 17·5 lbs. of chlorine.

63. "*Benzylidenecamphoroxime*." By M. O. FORSTER. An examination of α aminocamphoroxime, described by Lapworth and Harvey (*Proc. Chem. Soc.*, xviii., 70), appears to have been undertaken with the object of investigating changes which substituted camphoroximes undergo in virtue of the presence of the oximido-group. This has been the author's aim in his study of camphoroxime, which has extended over several years, and contributions to the chemistry of β -chlorocamphoroxime, β -bromocamphoroxime, and α -benzylidenecamphoroxime have been already made. As Lapworth and Harvey have notified privately their intention to abandon the investigation, the author wishes to intimate that he proposes to continue the study of substituted camphoroximes. The following observations relating to benzylidenecamphoroxime are now put on record.

Benzylidenecamphoroxime, $C_{17}H_{21}ON$, dissolves sparingly in boiling alcohol, and crystallises in transparent hexagonal prisms, melting at 107° ; for a 2 per cent solution in chloroform, $[\alpha]_D = +389^\circ$. The *benzoyl* derivative crystallises from petroleum in lustrous, well-formed prisms, and melts at $106-107^\circ$; for a 2 per cent solution in chloroform, $[\alpha]_D = +246^\circ$. The *phenylcarbamate* separates from alcohol in tufts of long, silky needles, and melts at 160° , when it evolves gas; a 2 per cent solution in chloroform has $[\alpha]_D = +275^\circ$. Nitrous acid converts benzylidenecamphoroxime into the compound $C_{17}H_{20}O_2N_2$, which melts at 117° , and gives Liebermann's reaction.

Attempts to convert the oxime into benzylidenecamphenonitrile by the agency of boiling sulphuric acid (25 per cent) have been unsuccessful, but acetyl chloride gives rise to a *nitrile* which is unsaturated and feebly laevorotatory.

The oxime is indifferent towards sodium amalgam, which reduces benzylidenecamphor to benzylcamphor, but sodium in boiling amyl alcohol reduces it to bases which probably represent the α -benzyl derivatives of bornylamine and neobornylamine; the *platinichloride* from the dextrorotatory hydrochloride melts at 235° , whilst the *platinichloride* from the laevorotatory hydrochloride melts at 247° .

ROYAL INSTITUTION. *Annual Meeting, May 1st, 1902.*

Sir JAMES CRICHTON-BROWNE, M.D., F.R.S., Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1901, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read.

Forty-four new Members were elected in 1901. Sixty-three Lectures and seventeen Evening Discourses were delivered in 1901. The Books and Pamphlets presented in 1901 amounted to about 253 volumes, making, with 722 volumes (including Periodicals bound) purchased by the Managers, a total of 975 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—The Right Hon. Lord Alverstone, Sir James Blyth, Bart., Sir Frederick Bramwell, Bart., Dr. Thomas Buzzard, Dr. Donald Hood, Sir Francis Laking, Mr. George Matthey, Dr. Ludwig Mond, Dr. Hugo Muller, Mr. Edward Pollock, Sir Owen Roberts, Sir Felix Semon, The Right Hon. Sir James Stirling, Mr. John I. Thornycroft, and Mr. James Wimshurst.

Visitors—Dr. Henry E. Armstrong, Dr. Charles Edward Bevor, Mr. John B. Broun-Morison, Mr. Francis Elgar, Mr. Francis Gaskell, Dr. Dundas Grant, Lord Greenock, Mr. Maures Horner, Sir Henry Irving, Mr. Wilson Noble, Mr. W. R. Pidgeon, Mr. Arthur Rigg, Mr. W. S. Squire, Mr. Harold Swithinbank, and Mr. Charles Wightman.

NOTICES OF BOOKS.

Lighting by Acetylene; a Treatise for the Practical Lighting Engineer. Containing Elementary Information and Details for those about to take up the Work. By FREDERICK DYE, M.R.I. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1902. Pp. 188.

THE purpose of this treatise is, firstly, to make clear what is good and bad in acetylene, or, in other words, to show how its good qualities can be obtained and bad ones avoided or not created; secondly, to be a practical guide to the engineer or fitter undertaking this work.

That Mr. Dye is an optimist as regards acetylene lighting is very evident from a perusal of this book, but we think he goes too far when he states:—"Acetylene can now be made (given a proper generator) by a lad or any unskilled person, without supervision, and with no risk"; and again, speaking of the generator, "it will need no more attention than can be given by a lad, farm-hand, or female servant; and the attendance need not exceed from five to ten minutes per day for a fair-sized plant." Now, a "farm-hand" is generally taken as representing a type of crass stupidity, and the idea of a "fair sized plant" being left to the tender mercies of such a man "without supervision" is at least startling. We may indeed ask, if the above statements are in any way true, why has the author taken the trouble to write this book as a practical guide to engineers and fitters? Surely they are as sharp as the average "lad, farm-hand, or female servant."

After an introduction giving an elementary description of the process of acetylene gas production, the author goes through the history of calcium carbide from which the gas is made. The properties of this gas, with its advantages, risks, &c., are fully described in Chapter II. The next two chapters are devoted to acetylene generators, with types and examples.

The principle of generating acetylene gas is one of the simplest known, yet it has resulted in a vast variety of generating apparatus, usually followed by their appropriate explosions. There are practically four methods now in use; first, that in which the carbide is dropped into water; second, that in which the carbide is placed in trays and the water allowed to drip on it as required;

third, that in which the carbide is put in a holder and dipped into the water, or has the water approach it for a few seconds, whenever the store of gas gets low; and fourth, that in which the carbide is placed in trays and the water allowed to flow to it (not on it), and in about sufficient volume for the quantity of carbide to be attacked. There are modifications of all these methods.

After production, acetylene requires purification, and too much importance cannot be attached to the bearing that generators have on the purity of the gas they produce. At one time the carbide bore all the blame, but now the case is different; experience has shown that the measures to be adopted towards securing pure gas are simply cool generation, and making the gas pass through water as fast as it is made. There are not many different means of purifying acetylene chemically at present, but those that are known are described in Chapter V.

Chapter VI. deals with burners and appliances. The perfect burner has yet to be designed; there are burners, of which the "Naphey" is a well known one, which consume the gas perfectly, but they all become choked with soot at some time. The chief detail of the Naphey burner, and the large number of others made on that principle, is the provision of air-holes leading from the exterior of the nipple to the mixing chamber, or hollow in the centre of the extreme tip; as the gas issues it draws in air which mixes with it, the result being a whiter flame, more perfect combustion, and freedom from smoke.

Chapter VII., and last, is on the legal and other regulations governing the storage of carbide and the fixing of acetylene generating apparatus.

A copy of a licence to keep or store calcium carbide, such as is issued by a country District Council, is given in full, and this represents the documents which lighting engineers are most likely to see, or have to work to, it is recommended that it be carefully read and its contents committed to memory as far as possible.

The book is clearly written and well illustrated, and will doubtless be of value to those connected with the subject of lighting by means of acetylene gas; it also appears to be efficiently indexed.

The Factory and Workshop Act, 1901. Its General Effect and Parliamentary History, with Notes and other Information (including the Full Text of the Act) for the Guidance of Employers of Labour and Others. By C. WILLOUGHBY WILLIAMS, B.A., and CHARLES E. MUSGRAVE. London: Effingham Wilson; and A. Stuart, Carthusian Press. 1902. Pp. 196.

THE FACTORY and Workshop Act of 1901 is a measure of considerable importance, and is an advance on previous legislation of a similar kind; it confirms and consolidates the bulk of the old law, and, at the same time, largely extends the State regulation of industry as regards health, sanitation, safety, hours of labour, and other matters. It also throws additional responsibilities upon the Home Office and the local sanitary authorities, and increases the statutory obligations of manufacturers in many material respects.

As the Act only came into operation on January 1st, 1902, any guide to it must be necessarily incomplete, and the authors do not claim to have done more than show, in simple language, its effect as a whole, the principal changes that have been made in the law, and the manner in which the measure passed through Parliament.

The text of the Act is reproduced in full, and the new or modified portions are, as far as practicable, printed in italics; this feature should be extremely useful.

The book is divided principally into three parts; Part I., on the Effect of the Act; Part II., on the Changes in the Law; and Part III. on the Parliamentary History of the Act; then follows the Act with notes and comments, the appendix, containing orders and special rules, and finally the index.

The importance of the interests involved are shown by

the report of the Chief Inspector of Factories and Workshops for the year 1900, in which it is stated that the number of factories on the registers was 95,664, and of workshops 137,648, all of which are affected by this change in the law.

E. Merck, Darmstadt. Annual Report on the Year 1901. Published March, 1902. Pp. 207.

THE annual report on the year 1901 follows in form that of previous years. At the commencement there is an exhaustive and detailed article giving the results of original investigations on opium tests.

The succeeding pages contain the usual epitome of the publications of many investigators, and take note of a large number of the recent materia medica. Among the most important items may be mentioned the cacodylates, which are attracting considerable attention at present.

Other preparations dealt with are aconitine, eumenol, tannoform, amyl salicylate, calcium glycerino-arsenate, and many more.

CORRESPONDENCE.

ARSENITE OF SILVER.

To the Editor of the Chemical News.

SIR,—Let me congratulate Mr. Wanklyn on his ability to perform an approximately accurate analysis of silver arsenite in the year 1902; but also let me protest against the libel on Charles L. Bloxam's analytical skill contained in Mr. Wanklyn's words "the drop in percentage of As_2O_3 from 25.88 to 22.19 might have been due to deposit of salt-petre or nitrate of silver in the precipitate!"—I am, &c.

A. G. BLOXAM.

Birkbeck Bank Chambers, W.C.,
May 5, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiv., No. 15, April 14, 1902.

Researches on Electromotive Forces.—M. Berthelot. —The author performs five series of experiments, from which he draws the conclusion that the electromotive forces, often considerable, which are developed by the union of a great number of elements in a pile, consist of simple actions of neutralisation or analogous reactions, under conditions which are described. These are often insufficient to produce appreciable phenomena of electrolysis, but are especially susceptible of intervening in physiological chemistry. The author also succeeds in making oxidising and reducing reactions take place in saline solutions of piles, and under conditions which he will further investigate, and which are evidently comparable in certain aspects to the reactions which take place during physiological phenomena.

Composition of Gaseous Hydrates.—M. de Forcrand. —In spite of the large number of researches on the subject, the composition of the hydrates of gases appears to be very difficult to determine directly. The author believes that the relation which he gives, $\frac{Q}{T} = 30$, in

which Q is the heat of formation of the solidified hydrate and solid water, and T the absolute temperature for which the hydrate has a tension of 760 m.m., allows of a very simple solution of the problem in a great number of cases,

Action of Hydrogen on Strontium Amalgam.—M. Guntz.—In a preceding paper the author shows that whilst heating strontium amalgam in a current of hydrogen, pure strontium hydride, SrH_2 , is obtained. He now further investigates the conditions of this reaction, and the precautions which must be taken to obtain the hydride free from mercury. A knowledge of the dissociation tensions of strontium hydride enables the exact conditions of preparation of metallic strontium from this compound to be found.

Compounds of Aluminium with Chromium Sesquioxide.—M. Duboin.—M. Lecoq de Boisbaudran established the conditions under which aluminium combines with chromium oxide, and concluded from his experiments that in rubies the chromium is present in the state of sesquioxide. The author now describes a means of separating the non-combined chromium oxide in these experiments. The oxide, if anhydrous, when heated for one and a-half hours at a white heat, rapidly and totally disappears in chlorate of potash, leaving alumina. By this means the proportion of chromium oxide which is combined with the alumina can be found.

Products of Decomposition of Amidotariric Acid.—M. Arnaud.—By heating amidotariric acid with fuming hydrochloric acid in sealed tubes at 170° , four products of decomposition are obtained. The separation of these bodies is very complicated: they are, on the one hand, undecylamine, $\text{C}_{11}\text{H}_{23}\text{NH}_2$, and pimelic acid, $\text{C}_7\text{H}_{12}\text{O}_4$; and, on the other hand, lauric acid, $\text{C}_{12}\text{H}_{24}\text{O}_2$, and ϵ -amidocaproic acid, $\text{C}_6\text{H}_{13}\text{NO}_2$. All these bodies were purified and analysed and numbers obtained agreeing with the above formulæ. As a result of this research the author is led to adopt for tariric acid the constitutional formula $\text{CH}_3-(\text{CH}_2)_{10}-\text{C}\equiv\text{C}-(\text{CH}_2)_4-\text{CO}_2\text{H}$.

Diacetylbenzoylthane and Acetylmethylphenylfurfurane.—F. March.—In a preceding paper the author describes the preparation of diacetylbenzoylthane or phenacylacetylacetone, to which he attributes the formula $(\text{CH}_3-\text{CO})_2=\text{CH}-\text{CH}_2-\text{CO}-\text{C}_6\text{H}_5$. He now further investigates this compound and its derivatives. Phenacylacetylacetone behaves either as a β -diketone or as a γ -diketone. As the former it combines with hydroxylamine, phenylhydrazine, and semicarbazide, forming the isoxazols and the pyrazols. As a γ -diketone it yields a product of dehydration by losing a molecule of water, this product being acetylmethylphenylfurfurane, and it combines with ammonia in alcoholic solution, giving rise to a phenyl-2-acetyl-4-methyl-5-pyrrol.

Methoethenylbenzene.—M. Tiffeneau.—The author investigates the benzenic carbides with methoethenyl chain, and compares their properties with those of other compounds corresponding to the lateral chain, C_3H_7 .

Oxyisopropylphosphinic Acid.—C. Marie.—Oxyisopropylphosphinic acid is formed when a mixture of hypophosphorous acid and acetone is boiled for some time. It is produced in this case by the slow oxidation of the acid $\text{PO}_2\text{H}_3\text{C}_3\text{H}_6\text{O}$ by means of the oxygen of the air. In consequence of the presence of small quantities of phosphorus and phosphoric acids in the products of this reaction, whose lead salts precipitate at the same time as that of the acid $\text{PO}_3\text{H}_3\text{C}_3\text{H}_6\text{O}$, this latter is difficult to purify completely. It has a fusion-point of $170-171^\circ$ lower than that of the acid prepared by the more complicated process described in detail in this paper.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th inst., The Duke of Northumberland, President, in the Chair. Dr. Alfred Hillier, Mr. Sydney Lupton, Mr. Carl F. von Siemens, and Mrs. C. F. von Siemens were elected Members. The special thanks of the Members were

returned to Sir Thomas Sanderson, G.C.B., K.C.M.G., for a donation of £5 5s. to the Fund for the Promotion of Experimental Research at Low Temperatures. The Chairman announced that His Grace the President had nominated the following Vice-Presidents for the ensuing year:—The Right Hon. Lord Alverstone, Sir Frederick Bramwell, Dr. Donald Hood, Mr. George Matthey, Dr. Ludwig Mond, The Right Hon. Sir James Stirling, Sir James Crichton-Browne, and Sir William Crookes.

Molybdc Acid.—P. Klason.—The author has repeated the analysis of ordinary molybdate of ammonium, and determined its molecular weight cryoscopically, and has found that its true formula should be $6\text{NH}_3 \cdot 6\text{MoO}_3 \cdot 5\text{H}_2\text{O}$; this salt may be regarded as intermediate between the di- and tri-ammonic trimolybdates. A salt described by Rammelsberg is in reality the tri-ammonic trimolybdate, $(\text{MoO}_4)_3(\text{NH}_4)_3\text{H}_3 + 4\text{H}_2\text{O}$; as for the di-ammonic trimolybdate, $(\text{MoO}_4)_3(\text{NH}_4)_2\text{H}_4 + \text{H}_2\text{O}$, it is formed by the addition of the calculated quantity of hydrochloric acid to a cooled solution of ordinary molybdate; after twenty-four hours a granular crystalline crust is formed, slightly soluble in the cold, and very soluble in warm water, but with decomposition. A mono-ammonic trimolybdate occurs under similar conditions, with the exception of a different quantity of hydrochloric acid; care must be taken to stir continuously, and to add the hydrochloric acid in a fine stream; before long a felted mass of fine needles is formed of the salt $(\text{MoO}_4)_3\text{NH}_4 \cdot \text{H}_5$, having properties similar to those of the preceding salt. Commercial "molybdc acid," answers as nearly as possible to the formula $\text{NH}_3 \cdot 3\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. By proceeding as with the other salts, that is by the addition of the calculated quantity of hydrochloric acid to a cooled solution of ordinary molybdate, then filtering after twelve hours to remove the slight turbidity, there are formed, after a few weeks, beautiful clear crystals of the salt $3\text{NH}_3 \cdot 6\text{MoO}_3 \cdot 5\text{H}_2\text{O}$, intermediate between the mono- and di-ammonic trimolybdates. Having observed that the phosphomolybdate of ammonium contained 12MoO_3 , the author tried, as in the case of the above-mentioned salts, whether he could not produce a tri-ammonic dodecamolybdate. The addition of an excess of hydrochloric acid to a solution of ordinary molybdate gave a white precipitate formed of very small hexagonal prisms of a tri-ammonic pentadecamolybdate, $3\text{NH}_3 \cdot 15\text{MoO}_3 \cdot 20\text{H}_2\text{O}$, soluble in boiling water; on evaporating at the ordinary temperature the salt re-crystallises without change, but very slowly. To dissolve this salt, it is necessary to plunge it suddenly into boiling water; otherwise, if we heat up gradually in the water, an altogether insoluble hydrate containing $6\text{H}_2\text{O}$ is formed; the same product is formed by the desiccation of the salt containing $20\text{H}_2\text{O}$, even at the ordinary temperature. The warm solution of the preceding salt, treated with sal-ammoniac, gives, on cooling, beautiful brilliant prisms of the tri-ammonic dodecamolybdate, $3\text{NH}_3 \cdot 12\text{MoO}_3 \cdot 12\text{H}_2\text{O}$. The author is of the opinion that all the molybdates, and without doubt even molybdc acid itself, contain the nucleus Mo_3 , and it is for this reason that he has not simplified some of the above formulæ; in fact, we get the chloride Mo_3Cl_6 , and not MoCl_2 .—*Berichte*, vol. xxxiv., p. 153.

MEETINGS FOR THE WEEK.

- TUESDAY, 13th.—Royal Institution, 3. "English Kings and Kingship," by Prof. F. York Powell, M.A., LL.D.
WEDNESDAY, 14th.—Society of Arts, 4.30. "Boats and Boat Building in the Malay Peninsula," by H. Warrington Smyth.
Royal Society Conversazione.
THURSDAY, 15th.—Royal Institution, 3. "Recent Geological Discoveries," by A. Smith Woodward, LL.D., F.R.S.
FRIDAY, 16th.—Royal Institution, 9. "The Nebular Theory," by Sir Robert Ball, M.A., LL.D., D.Sc., F.R.S.
SATURDAY, 17th.—Royal Institution, 3. "Poets and Poetry," by Prof. Walter Raleigh, M.A.

THE CHEMICAL NEWS.

VOL. LXXXV., No. 2216.

VOLUMETRIC ESTIMATION OF PEROXIDE OF LEAD IN MINIMUM.

By M. LIEBIG.

FOR many years past I have used the following method for the determination of the proportion of peroxide of lead in minimum. This method is very convenient, and can be generally recommended on account of the sharpness of the end of the reaction.

Half a gramme of finely powdered minimum is placed in a small Erlenmeyer flask, with a little distilled water. By means of a burette 25 c.c. of a decinormal solution of hyposulphite of soda are added, then 10 c.c. of about 30 per cent acetic acid. On well shaking, the mass goes into solution. Then add 10 c.c. of a solution of iodide of potassium at 10 per cent, 2 or 3 c.c. of a solution of iodide of zinc and starch, and titrate the excess of hyposulphite with a decinormal solution of iodine. By multiplying the number of c.c. of iodine used by 239 (239 is the molecular weight of peroxide of lead), we obtain the proportion of peroxide present in the minimum.

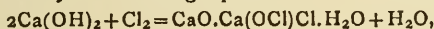
The end of the reaction is recognised by the change of colour caused by the iodide of lead formed from citron-yellow, as it is at first, to a deep dirty yellow.

As we have said, the reaction is very sharp and very rapid, and it is not necessary to have a very practised eye to perform the operation.—*Zeit. fur Angew. Chem.*, 1901, p. 528.

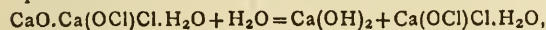
THE FORMATION AND COMPOSITION OF HYPOCHLORITE OF LIME.

By H. OITZ.

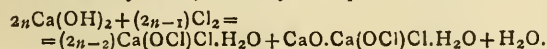
As a result of some experiments on the action of heat, and of dry and moist carbonic acid on several samples of hypochlorite of lime, the author concluded that the action of the chlorine on dry hydrate of calcium should be expressed by the following equation:—



but that the water formed tends to react according to the equation:—



allowing a fresh quantity of lime to react with the chlorine. The presence of moisture in the lime (due to the water used to slake it) tends to give more importance to the second reaction, and the general result of these successive reactions may be expressed by the equation:—



The composition of any sample of chloride should thus be comprised between the formulæ limits $\text{CaO} \cdot \text{Ca}(\text{OCl})\text{Cl} \cdot \text{H}_2\text{O}$ (35.32 per cent of chlorine) and $\text{Ca}(\text{OCl})\text{Cl} \cdot \text{H}_2\text{O}$ (48.96 per cent of chlorine). Neither one nor the other of these formulæ can be accepted as the constitution formula of the compound it represents. To decide on this constitution formula the following facts must be borne in mind:—1. The compound $\text{CaO} \cdot \text{Ca}(\text{OCl})\text{Cl} \cdot \text{H}_2\text{O}$, stable at 100°, gives off oxygen at a slightly higher temperature, but no chlorine; the residue, $\text{CaO} \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$, only loses its water at a red heat. 2. The other compound, of which the formula is probably $2[\text{Ca}(\text{OCl})\text{Cl} \cdot \text{H}_2\text{O}]$, when heated to 100° in a current of dry air, gives off chlorine and water.—*Zeit. fur Angew. Chem.*, vol. xiv., p. 105.

A NEW INVESTIGATION CONCERNING THE ATOMIC WEIGHT OF URANIUM.*

By THEODORE WILLIAM RICHARDS
and
BENJAMIN SHORES MERIGOLD.

(Continued from p. 224).

The Results of the Analyses of Uranous Bromide.

THE method of analysis has been already fully described.

The analyses recorded in the first series were made by adding an excess of silver nitrate to the solution of uranyl bromide. From the ratio of the observed weights of uranous bromide to argentic bromide, the molecular weight of uranous bromide was calculated, that of argentic bromide being assumed to be 187.885. From the results obtained from this preliminary series the weight of silver necessary to precipitate the bromine in 1 gm. of uranous bromide was calculated. In the subsequent determinations the exact weight of silver required was weighed out, as nearly as possible, and dissolved in pure nitric acid with suitable precautions to avoid loss. The exact end-point was reached by standard hundredth normal solutions of argentic nitrate and hydrobromic acid, by means of the nephelometer (Richards, *Proc. Amer. Acad. Arts Sci.*, 1894, xxx., 385; *Zeit. Anorg. Chem.*, 1895, viii., 269). After determining the end-point, a slight excess of argentic nitrate was always added, and the weight of the total argentic bromide determined. Thus from each of these analyses two distinct ratios were obtained as a basis for the calculation of the molecular weight of uranous bromide—the ratio of uranous bromide to argentic bromide, and that of uranous bromide to silver.

As would naturally be expected from the complexity of operations involved, determinations of the sodium in the filtrates from the argentic bromide gave unsatisfactory results. The large quantity of filtrate and wash-waters had to be evaporated to small bulk, the uranium precipitated, and the sodium determined in the residue. It seemed advisable to make a series of separate analyses for sodium only, and use the average percentage of sodium found as a constant correction. This method was used in the work upon cobalt and nickel (*Proc. Amer. Acad. Arts Sci.*, 1899, xxxiv., 339, 365).

Accordingly three alkali determinations were made, wholly in platinum, the material not coming in contact with glass at any time except during the original collection and weighing of the sublimed bromide. The sublimate was dissolved in pure water, in a platinum dish, and the uranium was precipitated with pure ammonium sulphide. The ammonium sulphide was freshly prepared for each analysis, wholly in platinum. It left no residue on evaporation in platinum. The precipitated sulphide was digested on the water-bath to expel most of the excess of ammonium sulphide, filtered through a platinum funnel, and the filtrate and wash-water evaporated to small bulk in a platinum dish. The sodium bromide was then converted to sodium sulphate and weighed. The following table contains the data and result:—

No.	Weight of uranous bromide.	Weight sodic sulphate obtained.	Equivalent weight of sodic bromide.	Per cent sodic bromide.
	Grms.	Grm.	Grm.	
1.	1.656	0.00092	0.00133	0.081
2.	2.629	0.00143	0.00207	0.079
3.	1.407	0.00121	0.00175	0.124

Average 0.095

The average of these three determinations, 0.095 per cent, is practically identical with the amount of sodic bromide found in the cobalt and nickel work, which was 0.10 per cent. The porcelain tubes used in this investigation were of the same manufacture as those used in the

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxvii., No. 14.

THE ATOMIC WEIGHT OF URANIUM.

O = 16.000; Ag = 107.93; Br = 79.955.

First Series (Preliminary).— $\text{UBr}_4 : 4\text{AgBr}$.

No. of analysis.	Total weight of uranous bromide + sodium bromide in vacuo.	Weight of uranous bromide corrected for NaBr.	Total weight of silver bromide in vacuo.	Weight of silver bromide corrected for NaBr.	Parts of uranous bromide equivalent to 100 parts argentic bromide.	Atomic weight of uranium.
	Grms.	Grms.	Grms.	Grms.	Grms.	
1.	2.20795	2.2058	2.97391	2.9699	74.272	238.36
3.	1.44321	1.4418	1.94272	1.9401	74.316	238.69
5.	1.40639	1.4050	1.89355	1.8910	74.299	238.56
6.	1.17607	1.1749	1.58396	1.5818	74.276	238.39
Average						238.50

Second Series.— $\text{UBr}_4 : 4\text{AgBr}$.

7.	1.80174	1.7999	2.42588	2.4226	74.296	238.54
8.	1.06723	1.0662	1.43713	1.4352	74.290	238.50
9.	1.85698	1.8551	2.50009	2.4967	74.302	238.59
Average						238.54

Third Series.— $\text{UBr}_4 : 4\text{Ag}$.

No. of analysis.	Weight of uranous bromide with all corrections.	Weight of silver <i>in vacuo</i> (not corrected for sodic bromide).	Weight of silver with all corrections.	Weight of uranous bromide corresponding to 100 grms. silver.	Atomic weight of uranium.
	Grms.	Grms.	Grms.	Grms.	
10 (7).	1.7999	1.39365	1.3918	129.322	238.49
11 (8).	1.0662	0.82559	0.8245	129.315	238.46
12 (9).	1.8551	1.43617	1.4342	129.347	238.60
Average					238.52

Average of all determinations 238.52
 Average of six final determinations 238.53

nickel and cobalt work, and since the method of preparation of the three bromides was practically the same, probably the quantity of sodium extracted from the tubes by the action of the hot bromine vapour was the same—on the average—in all three cases, and not far from 0.10 per cent. Consequently, in calculating the following results, this value was used as a constant correction. The effect of applying the correction is to raise the calculated atomic weight about two-tenths of a unit. Of course, by this method the quantity of sodic bromide calculated will vary somewhat from the exact quantity present in individual determinations. The average result, however, will undoubtedly vary but little from the result obtained if the alkali could be determined in each sample. It certainly is very much nearer the truth than the results to be obtained by the cumbersome method of determining the alkali in the filtrate from each precipitation of argentic bromide.

Analysis No. 2 was rejected on account of contamination of the uranous bromide by shreds of asbestos from the packing of the jacket, and No. 4 was not used because the combustion-tube cracked during sublimation, rendering probable the formation of some oxybromide. The silver required in Analysis No. 6 was determined for practice preparatory to the final series, being 0.9087 grm. when all corrections were applied. It is not included in the table, since its nature was essentially preliminary. As usual, all weighings were reduced to the vacuum standard. While all the weighings were actually made to the hundredths of a milligram, the final corrected data are rounded off to the nearest tenth of a milligram, since the deviations of the results show that the hundredths could have had no significance.

The extreme difference between the highest and the lowest values in the preliminary series is 0.33 unit, in the second series 0.09 unit, and in the third series 0.14 unit. At first sight these variations seem large, but their relative magnitude appears smaller when the great molecular weight of uranous bromide, 558.34, is taken into consideration. Thus the extreme percentage error of the preliminary series is 0.06, while those of the last two series are only

0.016 and 0.024 per cent respectively. The so-called "probable error" of the average atomic weight computed from the six analyses numbered 7 to 12 inclusive, if each is given the same weight, is 0.015. That is, according to the theory of least squares, the atomic weight of uranium should be between 238.515 and 238.545.

The magnitude of the maximum deviations in these two final series is, moreover, about as large as would have been expected from known analytical uncertainty. The observed variation in the amount of sodic bromide, for which a constant correction had to be applied, would account for three-quarters of it, and the rest, corresponding to less than the tenth of a milligram in the weighings, might easily be due to unavoidable errors of weighing or manipulation.

Further evidence of the trustworthiness of the figures is to be found in the comparison of the amounts of silver used in Analyses 10, 11, and 12, with the corresponding amounts of argentic bromide, found in Analyses 7, 8, and 9. This comparison is given in the following table, which gives the weights of silver corresponding to 100,000 parts of argentic bromide.

Weight of AgBr in vacuo.	Weight of Ag in vacuo.	Quotient $\times 100 =$ per cent of silver in argentic bromide.
Grms.	Grms.	
2.42588	1.39365	57.449
1.43713	0.82259	57.447
2.50009	1.43617	57.445
Average		57.447
Stas found		57.445

The result not only verifies the mechanical work, but affords evidence that the precipitate must have been pure argentic bromide. Clearly, then, the analysis is as accurate as need be. Further repetition of the process might reduce the so-called "probable error," but could not change the average by a significant amount. In the present state of the question, the method seems to have been carried as far as expediency demands.

(To be continued).

CHEMICAL SOCIETIES OF THE NINETEENTH CENTURY.*

By HENRY CARRINGTON BOLTON, Ph.D.

(Continued from p. 221).

FRANCE.

SOCIÉTÉ INDUSTRIELLE DE MULHOUSE.

FOUNDED in December, 1825, at Mulhouse (first meeting, May 11, 1826). In 1900: President, Auguste Dollfus; honorary members, 9; resident members, 190; non-resident members, 378; correspondents, 54.

Publication.—Bulletin de la Société industrielle de Mulhausen (*sic*), 1827-1900.

NOTE.—This is not purely a chemical society, but has a Committee on chemistry, and its Bulletin contains many papers on applied chemistry.

SOCIÉTÉ CHIMIQUE DE PARIS.

Founded June 4, 1857, at Paris. In 1900: President, Edouard Grimaux; members, 365; patrons, 121; life members, 91; corresponding members, 449.

Publications.—(a) Bulletin des séances de la Société chimique de Paris, 1858-62; (b) Répertoire de chimie pure et appliquée, 1858-63; (c) Bulletin de la Société chimique de Paris, 1864-1900; (d) Conférence et Leçons, 5 vols.

ASSOCIATION DES ÉLÈVES DE M. FREMY.

Founded in 1878 at Paris. In 1900: President, Louis Barthélemy; members, 200.

Publication.—Bulletin trimestriel de l'Association des élèves de M. Fremy, 1878-1900.

NOTE.—A social organisation, which, however, publishes the work of its members.

ASSOCIATION DES CHIMISTES DE SUCRERIE ET DE DISTILLERIE DE FRANCE ET DES COLONIES.

Founded in 1883 at Paris. In 1900: President, M. Durin; honorary members, 3; resident members, 160; non-resident members, 710; corresponding members, 395.

Publication.—Bulletin de l'Association des Chimistes de sucrerie et de distillerie de France et des Colonies, 1883-1900.

ASSOCIATION AMICALE DES ANCIENS ÉLÈVES DE L'ÉCOLE DE PHYSIQUE ET DE CHIMIE INDUSTRIELLE DE LA VILLE DE PARIS.

Founded in 1885 at Paris. In 1900: President, Octave Boudouard; honorary members, 41; members, 300.

Publication.—Bulletin mensuel de l'Association amicale des anciens élèves de l'Ecole de physique et de chimie industrielle de la ville de Paris, 1885-1900. Annuaire (&c.), 1885-1900.

ASSOCIATION AMICALE DES ANCIENS ÉLÈVES DE L'ÉCOLE DE CHIMIE INDUSTRIELLE DE LYON.

Founded in 1886 at the Institut chimique de Lyon. In 1900: President, Alphonse Seyewitz; honorary members, 6; members, 104.

Publication.—Bulletin des séances de l'Association amicale des anciens élèves de l'Ecole de chimie industrielle de Lyon.

SYNDICAT CENTRAL DES CHIMISTES ET ESSAYEURS DE FRANCE.

Founded in 1890 at Paris. In 1900: President, Ferdinand Jean; members, 125.

Publications.—Revue de chimie analytique appliquée à l'industrie, 1893-98. Annales de chimie ana-

lytique appliquée à l'industrie became the organ of the society in 1899; the Annales had been established in 1896, and was united with the Revue (above named) in 1899.

SOCIÉTÉ CHIMIQUE DU NORD DE LA FRANCE.

Founded at Lille in 1891. In 1900: President, A. Pouriez; members, 100.

Publication.—Bulletin mensuel de la Société chimique du Nord de la France, 1891-1900.

ASSOCIATION AMICALE DES ANCIENS ÉLÈVES DE L'INSTITUT CHIMIQUE DE NANCY.

Founded November 9, 1892, at Nancy. In 1900: President, M. Noel; honorary members, 8; patrons, 7; members, 52; associates, 75.

Publication.—Bulletin (annuel) de l'Association.

ASSOCIATION AMICALE DES ÉLÈVES ET ANCIENS ÉLÈVES DU LABORATOIRE D'ENSEIGNEMENT PRATIQUE APPLIQUÉE DE L'UNIVERSITÉ DE PARIS.

Founded in 1897 at Paris. In 1900: President, M. Loyer; honorary members, 12; members, 110.

Publication.—Gazette de chimie, Paris, 1900.

GERMANY.

VEREIN FÜR DIE RÜBENZUCKER INDUSTRIE IM ZOLLVEREIN (later, DES DEUTSCHEN REICHS; later, VEREIN DER DEUTSCHEN ZUCKERINDUSTRIE).

Founded in 1850 at Berlin. In 1900: President, De Coste; members, 447.

Publication.—Zeitschrift des Vereins (&c.), 1850-1900.

DEUTSCHE CHEMISCHE GESELLSCHAFT ZU BERLIN.

Founded in 1867 at Berlin. In 1900: President, G. Volhard; honorary members, 15; life members, 92; members, 2637; associates, 372.

Publication.—Berichte der deutschen chemischen Gesellschaft zu Berlin, 1868-1900. Since 1897 also Chemisches Centralblatt (established in 1830).

VEREIN ANALYTISCHER CHEMIKER.

Founded in 1878 at Magdeburg, and merged in 1887 with the Deutsche Gesellschaft für angewandte Chemie. See Verein deutscher Chemiker.

Publication.—Correspondenzblatt des Vereines analytischer Chemiker, 1878-80.

FREIE VEREINIGUNG BAYERISCHER VERTRETER DER ANGEWANDTEN CHEMIE.

Founded in May, 1883, at Munich. In 1900: President, Albert Hilger; honorary members, 2; members, 124; correspondents, 69.

Publications.—Bericht über die 1 (-18) Versammlung der freien Vereinigung bayerischer Vertreter der angewandten Chemie, 1883-1900. Also reports in Forschungsberichte über Lebensmittel und ihre Beziehung zur Hygiene, 1894-97; and in Zeitschrift für Untersuchung der Nahrungs- und Genuss-Mittel, 1898-1900.

VEREIN DEUTSCHER BERUFS-CHEMIKER.

Founded in 1887 at Dresden.

Publication.—The "Chemiker und Drogist" (Dresden, 1885) had in 1887 the sub-title Correspondenzblatt des Vereins deutscher Berufs Chemiker. This title was dropped in 1888.

DEUTSCHE GESELLSCHAFT FÜR ANGEWANDTE CHEMIE.

Founded November, 1887, at Berlin, absorbing the Verein analytischer Chemiker. In 1896 the Society became Verein deutscher Chemiker, q. v.

* Read at the Twenty-fifth Anniversary of the American Chemical Society, held in New York City, April 12-13, 1901. From advance proofs of the *Smithsonian Miscellaneous Collections*, 1901.

Publication.—Zeitschrift für angewandte Chemie, 1888-1900. This was begun as Zeitschrift für die chemische Industrie in 1887.

VEREINIGUNG ÖFFENTLICHER ANALYTISCHER CHEMIKER SACHSENS.

Founded in 1890 at Plauen in Vogtland. In 1900: President, Arthur Forster; members, about 25.

Publication.—Zeitschrift für öffentliche Chemie, 1897-1900. Also Bericht über die Hauptversammlung des Vereines öffentlicher analytischer Chemiker Sachsens.

VEREIN AKADEMISCH-GEBILDETE (ATER, DEUTSCHER) ZUCKERTECHNIKER.

Founded in 1891 at Berlin. In 1900: President, H. Claassen; honorary members, 1; members, 406; correspondents, 3.

Publication.—Zeitschrift des Vereines akademisch-gebildete Zuckertechniker, 1891-92.

NOTE.—The organ of publication changed several times.

VERBAND DES LABORATORIUMS-VORSTÄNDE VON DEUTSCHEN HOCHSCHULEN.

Founded in 1898 (?).

ZWEIGVEREIN DER ZUCKERTECHNIKER FÜR DAS AUSLAND.

Founded at Berlin. In 1901: President, C. Huck.

DEUTSCHE ELEKTROCHEMISCHE GESELLSCHAFT.

Founded in October, 1894, at Berlin. In 1900: President, J. H. van 't Hoff; members, about 700.

Publication.—Bericht der deutschen elektro-chemischen Gesellschaft, 1894-1900.

VEREIN DEUTSCHER CHEMIKER.

Founded in 1896 at Berlin, as successor to Gesellschaft für angewandte Chemie (1887). Its seat is the residence of the President for a given year. In 1900: President, H. Caro; honorary members, 4; members, 2271. Embraced in 1900 the following sections (Bezirk-Vereine):—Aachen, Belgien, Berlin, Frankfurt, Hamburg, Hannover, Mittel-Franken, Mittel- und Niederschlesien, Oberhein, Oberschlesien, Pommern, Rheinland, Rheinland-Westphalen, Saar, Sachsen-Anhalt, Sachsen-Thüringen, Württemberg.

Publication.—Zeitschrift für angewandte Chemie, 1887-1900. Cf. Deutsche Gesellschaft für angewandte Chemie.

VERBAND SELBSTÄNDIGER ÖFFENTLICHER CHEMIKER DEUTSCHLANDS.

Founded May 30, 1896, at Nürnberg. In 1900: President, Robert Kayser; members, 161; Associates, 102.

Publication.—Zeitschrift für öffentliche Chemie (established in 1895), 1897-1900. Also Vol. I. as Vol. III., 1897, of Centralblatt für Nahrungs- und Genussmittel Chemie, sowie Hygiene.

(To be continued).

The Estimation of Chromium and Iron by a Mixture of Iodide and Iodate of Potassium.—A. Stock and C. Masaciu.—The method in question has already been applied by M. Stock (*Berichte*, vol. xxxiii., p. 548) to the estimation of aluminium, and gave better results than the precipitation by ammonia. To the solution of chromium or iron (FeO or Fe_2O_3), slightly acidulated, an excess of a mixture of iodide and iodate of potassium is added, then, after a few minutes, hyposulphite of soda is added to decolorise the iodine set free; a few more cubic centimetres of this salt are then added, and the liquid, with the precipitate in suspension, is boiled for half-an-hour. The precipitate is collected on a filter in a warm funnel, then washed, dried, and weighed.—*Berichte*, vol. xxxiv., p. 467.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, April 30th, 1902.

Prof. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Percy J. Ferris, Heathfield, Seymour Grove, Old Trafford, Manchester; Alexander Gow, 38, Clarendon Street, Cambridge; Archie Cecil Osborn Hann, 54, Wood Vale, Forest Hill, S.E.; Walter Ernest Harrison, 43, Mostyn Road, Handsworth, Staffs.; Sinnott Valentine O'Connor, 14, Selskar Street, Wexford; Stephen Jamieson Ralph, 22, Stanley Place, Eccleston Square, S.W.; Edwin Ralph, Hong-Kong.

A ballot for the election of Fellows was held, and the following were declared duly elected:—James Samuel Ashe; Frederic Guy S. Baker, B.A.; Cyril Bergtheil; Richard Blenkinsop; Ernest Boardman, B.Sc.; Alexander Bruce, B.Sc.; Fred. Carodius; G. H. A. Clowes, Ph.D.; Arthur James Cook; James Codrington Crocker, B.A.; Henry Crookes; Charles Benson Davis; Henry Arthur Dobson; Walter Everitt; J. Arthur Gill; John T. Griffiths; Gilbert Gunn; Arthur Hopwood; Frank Eustace King, B.Sc.; Sidney Isaac King; James Kewley, B.A.; A. Lionel Landau; C. H. Lockitt, B.A.; Alexander Macknight; William H. Martindale, Ph.D.; Robert Mathieson; George A. H. Mence, B.Sc.; John Wicliffe Peck; Walter Ramshaw; Cecil Revis; Jonathan Hugh Roberts, B.A.; William Scholes; Thomas Taylor; Arthur Lea B. Tindall, M.A.; Stephen Herbert Trimen; William Wright Tunnicliffe; William Charles Wain; Edward John Wilkinson; Frank Stanley Wood; Thos. A. Young.

Of the following papers, those marked * were read:—

*64. "The Preparation of Absolute Alcohol from Strong Spirit." By S. Young, D.Sc., F.R.S.

The strongest spirit that can be obtained by distillation with the most perfect still-head contains less than 96 per cent by weight of pure alcohol. In order to remove the remainder of the water, dehydrating agents have always been employed, but they do not give very satisfactory results; according to Mendeleeff, freshly ignited lime is the only one by means of which pure dry alcohol can be prepared, and even with this substance special precautions have to be taken to ensure success. More recently, Squibb has obtained alcohol of still lower specific gravity by the long continued action of lime in a percolator, but his results, unlike those of Mendeleeff, were somewhat variable.

The method of dehydration recommended by the author depends on the fact that when a mixture of alcohol, benzene, and water is distilled, separation tends to take place into (1) a ternary mixture of alcohol, benzene, and water boiling constantly at 64.85° ; (2) one of three possible mixtures of constant boiling-point, (a) alcohol-benzene, b. p. 68.25° ; (b) benzene-water, b. p. 69.25° ; (c) alcohol-water, b. p. 78.15° ; (3) one of the three pure substances, alcohol, b. p. 78.3° ; benzene, b. p. 80.2° ; water, b. p. 100° .

For example, when a mixture of equal weights of 93 per cent alcohol and benzene is distilled, the fractions are (1) the ternary mixture containing, theoretically, the whole of the water; (2) the binary alcohol-benzene mixture; (3) pure alcohol.

Pure benzene and dilute alcohol are easily recovered from the ternary and binary mixtures, and there is practically no loss of material.

Theoretically, a single distillation should be sufficient to remove the whole of the water, but the separation is a difficult one, and even with a very efficient still-head a second, or even third, distillation with more benzene is necessary; the water may thus be completely eliminated,

but there appears to be a trace of benzene left in the alcohol. This trace of benzene may be completely removed by distillation of the dehydrated alcohol with *n*-hexane; the binary hexane-alcohol mixture which comes over first carries the benzene with it, and no hexane is left in the residual alcohol.

The observed specific gravities of dehydrated alcohol are as follows:—

Mendeleeff, by means of lime.. ..	0.80625 at 0°/4°
Young, by means of benzene	0.80634 "
" " benzene and hexane	0.80627 "

*65. "On the Properties of Mixtures of the Lower Alcohols with Water." By S. YOUNG, D.Sc., F.R.S., and Miss E. C. FORTEY, B.Sc.

Methyl alcohol does not form a mixture of minimum boiling-point with water, and, contrary to general opinion, dry methyl alcohol can be easily obtained by distillation of the dilute alcohol with an efficient still-head. The alcohol so obtained is drier than when the strongest dehydrating agents are used.

As regards the purification of the other six alcohols investigated, distillation with benzene gave the best results with ethyl, isopropyl, *n*-propyl, and tertiary butyl alcohols; this treatment was also found useful in the case of isobutyl and isoamyl alcohols for the removal of lower homologues. All these alcohols were found to form mixtures of minimum boiling-point with water. The boiling-points and the composition of these mixtures of constant boiling-point were determined, also the contraction which occurs on mixing the alcohols with water in various proportions, and the approximate temperature changes for certain mixtures. It was found that (a) the differences in boiling-point between the alcohol and the alcohol-water mixtures of constant boiling-point, (b) the molecular percentages of water in these mixtures, follow the same order as the boiling-points of the alcohols themselves. So far as experiments have been made, the heat evolution diminishes or the heat absorption increases as the boiling-points of the alcohols rise.

As regards the primary alcohols, the percentage contractions on mixing with water diminish as the boiling-points of the alcohols rise, but irregularities were observed with the secondary and the tertiary alcohols investigated.

The experiments show that as the molecular weights of the alcohols increase, the attractions of their molecules for those of water diminish, but the constitution as well as the composition of the alcohols must be taken into account. The constant boiling-point mixtures which the alcohols form with water are in no case hydrates of the alcohols.

*66. "On the Properties of Mixtures of the Lower Alcohols with Benzene and with Benzene and Water." By S. YOUNG, D.Sc., F.R.S., and Miss E. C. FORTEY, B.Sc.

Of the seven alcohols examined, all except isoamyl alcohol form mixtures of constant boiling-point with benzene. The boiling-points of these mixtures and the molecular percentages of benzene in them follow the same order as the boiling-points of the pure alcohols. The boiling-point of the isobutyl alcohol-benzene mixture is very near that of benzene itself; neither isoamyl alcohol nor any other alcohol with a higher boiling-point can form a mixture of constant boiling-point with benzene.

Of these alcohols, only ethyl, isopropyl, *n*-propyl, and tertiary butyl alcohols form ternary mixtures of constant boiling-point with benzene and water. When a mixture of methyl alcohol, benzene, and water is distilled, the first fraction consists of the binary alcohol-benzene mixture, and when a mixture of either isobutyl or isoamyl alcohol with benzene and water is distilled, the first fraction consists of the binary benzene-water mixture. No alcohol of this series with a boiling-point higher than that of isobutyl alcohol can form a ternary alcohol-benzene-water mixture of minimum boiling-point; with

these higher alcohols, the first fraction will always consist of the binary benzene-water mixture.

The boiling-points and the composition of the binary alcohol-benzene and the ternary alcohol-benzene-water mixtures have been determined.

*67. "Fractional Distillation as a Method of Quantitative Analysis." By S. YOUNG, D.Sc., F.R.S., and Miss E. C. FORTEY, B.Sc.

It has already been pointed out (Young, *Journ. Soc. Chem. Ind.*, 1900, xix., 1072) that the composition of a mixture of two homologous substances can be ascertained with a fair degree of accuracy from the results of one or more fractional distillations with a very efficient still-head without bringing about anything like a complete separation of the components.

The method has now been found applicable, not only to mixtures which separate normally into their original components, whether homologous or not, but also to cases in which binary or ternary mixtures of constant boiling-point are formed, such mixtures behaving, as regards distillation, like pure substances. It depends on the following facts:—In the case of a mixture which tends to separate into two components, the weight of distillate that comes over below the temperature midway between the boiling-points of the two components—whether single substances or mixtures of constant boiling-point—is almost exactly equal to that of the more volatile component. If the original mixture tends to separate into more than two components, the weight of these components will be very nearly equal to the weight of distillate below the first middle point, the weights of distillates between the successive middle points, and the weight above the last middle point respectively.

When a binary mixture of constant boiling-point is formed, the method may be employed for the determination of its composition if that of the original mixture is known, or of the original mixture if that of the binary mixture is known; when the original mixture tends to separate into a ternary mixture, a binary mixture, and a single substance, the composition of the ternary mixture may be ascertained, if that of the binary mixture and of the original mixture are known.

There are a few cases such as that of ethyl alcohol and water, or of benzene and *n*-hexane, to which the method is not applicable. In these, the curve representing the relation between boiling-point and molecular composition is exceedingly flat where the more volatile component is in large excess. When this is so, the separation by fractional distillation of the more volatile component, whether a single substance or a mixture of constant boiling-point, is practically impossible.

*68. "On the Vapour Pressures and Boiling-points of mixed Liquids." By S. YOUNG, D.Sc., F.R.S.

The question as to what should be regarded as the normal behaviour, with reference to their vapour pressures and boiling-points, of mixtures of two liquids soluble in each other in all proportions, has been discussed by several investigators.

It seemed probable that the simplest possible relations would be observed in the case of two such closely related substances as chlorobenzene and bromobenzene, the critical points of which are the same, whilst the ratio of the boiling-points on the absolute scale is constant at all equal pressures. Other simple physical relations exist between these substances, and no perceptible heat change or volume change occurs on mixing them.

The boiling-points of several mixtures of chlorobenzene and bromobenzene were determined over a range of about 100 m.m., and the results are in accurate accordance with the law which Van der Waals states should hold good for two liquids the critical points of which are equal, and for which $a_{1,2} = \sqrt{a_1 a_2}$ (Galitzine, Berthelot), where $a_{1,2}$ represents the mutual attraction of the unlike molecules and a_1 and a_2 the attractions of the like molecules.

The law may be stated thus:—The relation between the vapour pressures and the molecular composition of mixtures of such substances is represented by a straight line; or $P = \frac{p \cdot P_A + (100 - p)P_B}{100}$, where P , P_A , and P_B are the vapour pressures of the mixture, and of the two pure components, A and B, at the same temperature, and p is the molecular percentage of one of them.

*69. "The Correction of the Boiling-points of Liquids from Observed to Normal Pressure." By S. YOUNG, D.Sc., F.R.S.

Crafts (*Ber.*, 1887, xx., 709) gave a convenient table for the correction of the boiling-points of liquids from observed to normal pressure. There are, however, a few misprints in the table, and since then accurate determinations of the vapour pressures of a large number of pure substances have been made; it therefore seems desirable to give a revised and enlarged table for reference.

Crafts gave mean values of $\frac{\Delta t}{\Delta p} \cdot \frac{1}{T}$ for pressures between 720 and 770 m.m., but it seems more convenient, on the whole, to give the values of $\frac{dt}{dp} \cdot \frac{1}{T} = C$ at 760 m.m.

Various relations exist between the values of C and the chemical composition and constitution of the substances considered, and there is clearly a connection between the variations in the values of C and of other constants which have been considered in previous papers, such as $\frac{D_c}{D}$, the ratio of the actual to the theoretical density at the critical point.

*70. "Vapour Pressures and Specific Volumes of Isopropyl Isobutyrate." By S. YOUNG, D.Sc., F.R.S., and Miss E. C. FORTEY, B.Sc.

By the electrolysis of potassium isobutyrate, the yield of diisopropyl was found to be very poor, but a fair quantity of isopropyl isobutyrate was obtained. As this ester contains two *iso*-groups, it was thought that it would be of interest to determine its vapour pressures, specific volumes, and critical constants. For the sake of comparison, a second specimen of the ester was prepared from isopropyl alcohol and isobutyric acid, and the boiling-points and specific gravities of the two specimens were found to agree perfectly.

Unfortunately, isopropyl isobutyrate is much less stable than any of the ten esters previously examined (Young and Thomas, *Trans.*, 1893, lxiii., 1191), for some decomposition takes place at 230°, and the rate of decomposition increases rapidly with rise of temperature. It was therefore impossible to make trustworthy determinations of the critical temperature or pressure, so only the vapour pressures and specific volumes at and below 230° are given.

DISCUSSION.

Professor THORPE said, in reference to the observations which had been made by the author concerning the properties of the hydrated alcohols, and the thermal disturbance and alteration in volume accompanying the admixture of alcohols with water, that it appeared to be a tradition in the Revenue Service that on mixing ordinary (ethyl) alcohol and water, the combination, or association, of water and alcohol was only completed after a certain lapse of time, or, in other words, the mixture required to stand for some time before it acquired a constant volume, or, what comes to the same thing, a constant relative density. On what experimental evidence this belief was based was unknown to him, and direct observation made under his direction in the Government Laboratory, by Mr. John Holmes, showed that in reality the tradition had no foundation in fact. It probably had its origin in a statement in the original paper by Blagden and Gilpin that the mixtures of alcohol and water employed by them in their classical experiments, when made, were set aside for

some months, in order that, as stated by them, the "interpenetration" of the parts should be complete. It seems to have been taken for granted, in fact, that interpenetration, as something apart from complete and uniform miscibility, occurred on admixture, and that this operation required a certain and considerable interval of time.

The observation on the solubility of copper sulphate in methyl alcohol had been frequently made, and he believed some reference was made to it in a paper by the late Mr. Rodger and himself (*Phil. Trans.*, 1894, clxxxv., 530). According to Forcrand, the bluish compound has the composition $\text{CuSO}_4 \cdot 2\text{CH}_3\text{OH}$.

Some years ago, he made the observation that a mixture of carbon tetrachloride and methyl alcohol could be obtained which boiled several degrees lower than the boiling-point of the more volatile constituent. He had studied the relation between the boiling-point and composition of the mixture, determining the composition from the vapour density of the fractions (*Trans.*, 1879, xxxv., 544). He would be interested to know how far the quantitative results he had obtained were in conformity with the relations indicated by Dr. Young in the case of other mixtures of miscible liquids.

Mr. PICKERING said that although the existence of a constant boiling-point mixture of two substances cannot be taken as proof that these two substances are combined, yet the fact that the composition is affected to a certain extent by pressure is no proof of the contrary. Aqueous solutions of hydrochloric acid can be distilled unchanged when the composition is approximately $\text{HCl} \cdot 8\text{H}_2\text{O}$, and Roscoe and Dittmar were held to have disproved the existence of any such hydrate by showing that the composition is affected by pressure; yet, Berthelot proved that this variability did not by any means negative the existence of a hydrate, the mixture in question being one of comparative, though not of absolute, constancy. Indeed, we could not expect the composition to be unaffected by pressure, unless the compound were perfectly stable, and there were no products of its dissociation present.

The fact, also, that water can be crystallised from a solution does not in any way disprove the existence of a hydrate in solution. The water may be present only as one of the dissociation products of the hydrate, and whether it or the hydrate separates out depends on the circumstances of the crystallisation. Numerous instances in point might be given: thus, water may be crystallised from a 20 per cent solution of sodium hydroxide, though such a solution will, under other conditions, yield crystals of the heptahydrate, of which it is chiefly composed.

Dr. DIVERS mentioned, in connection with the author's account of the solution of anhydrous copper sulphate, with blue colour, in anhydrous methyl alcohol, that W. Wislicenus and Stoeber had recently pointed out (*Ber.*, 1902, xxxv., 540) that anhydrous cupric acetate dissolves in methyl alcohol when boiled with it, giving a deep green solution which deposits crystalline cupric methoxide-acetate, $\text{CH}_3\text{OCu} \cdot \text{C}_2\text{H}_3\text{O}_2$, if the boiling be prolonged.

Professor YOUNG replied that they had not yet investigated the mixture of carbon tetrachloride and methyl alcohol, but agree that it would be interesting to determine the composition of the mixture of minimum boiling-point by the distillation method, in order to compare the result with that obtained by Professor Thorpe from the vapour density.

He did not regard the variability of the composition of the mixtures of minimum boiling-point with the pressure as a sufficient proof, but only as strong confirmatory evidence as to the non-existence of hydrates of the alcohols. The reasons for believing that such hydrates do not exist are fairly numerous, whilst the only ground for assuming that the liquids under consideration are hydrates seems to be that they boil at a constant temperature. Yet the very fact that the boiling-points are lower than those of the alcohols themselves or than that of water indicates that the attraction of the unlike molecules is small compared with the attractions of the

like molecules, and this could hardly be the case if hydrates were formed. With regard to the interesting action of anhydrous copper acetate on methyl alcohol, he might mention that Beilstein describes a crystalline alcoholate of copper sulphate, $\text{CuSO}_4 \cdot \text{CH}_3\text{OH}$.

*71. "The Preparation of Highly Substituted Nitroaminobenzenes." By K. J. P. ORTON.

The methods at present known of preparing nitroaminobenzenes from anilines are scarcely applicable when the anilines possess two ortho-substituents. The following procedure has been devised, and in most cases gives a quantitative conversion of the aniline into the nitroamine.

To a solution of the aniline (1 part) in glacial acetic acid (25 parts) is added nitric acid (sp. gr. 1.5; 0.75 to 1 part); acetic anhydride (0.75 to 1 part) is slowly added to the cooled mixture. Heat is developed, and the aniline nitrate dissolves, forming a solution of the nitroamine.

By this means, the following nitroamines have been prepared:—

1-Nitroamino-3-tribromobenzene and 1-nitroamino-5-trichlorobenzene (*Proc.*, xviii., 58); 1-nitroamino-2:6-dichloro-4-bromobenzene, and 1-nitroamino-2:4-dichloro-6-bromobenzene, $\text{C}_6\text{H}_2\text{Cl}_2\text{Br} \cdot \text{NHNO}_2$, 1-nitroamino-2-chloro-4:6-dibromobenzene, and 1-nitroamino-4-chloro-2:6-dibromobenzene, $\text{C}_6\text{H}_2\text{ClBr}_2 \cdot \text{NHNO}_2$; these four substances crystallise in needles (from water), and all melt and decompose at 136–138°; their barium salts crystallise in plates with rH_2O . The N-methyl ether of nitroamino-5-tribromobenzene, $\text{C}_6\text{H}_2\text{Br}_3 \cdot \text{NMeNO}_2$, obtained from the sodium salt and methyl iodide, forms four-sided prisms melting at 95.5°.

1-Nitroamino-2:4-dibromo-6-nitrobenzene,—



m. p. 91–92°, forms yellow plates (from water); 1-nitroamino-2:3:4:6-tetrabromobenzene, plates melting and decomposing at 136°; 1-nitroamino-2:4:6-tribromo-3-nitrobenzene, yellow four-sided prisms, melting and decomposing at 108–109°; 1-nitroamino-2:4-dichlorobenzene, lustrous leaflets from petroleum, melting at 55–56°. The barium salt of the last-mentioned substance crystallises in plates with $\frac{3}{2}\text{H}_2\text{O}$.

4-Nitroamino-3:5-dibromotoluene,—



forms slender needles melting and decomposing at 122–123°; 2-nitroamino-3:5-dibromotoluene, needles, melting at 112°, and decomposing at 122°; the barium salts from each substance crystallise with rH_2O .

When nitroamino-5-trisubstituted benzenes contain a bromine atom in the para-position relative to the $\cdot\text{NHNO}_2$ group, the nitro-group is capable of displacing the β -bromine atom, giving a di-*o*-substituted β -nitroaniline. The majority of these nitroamines dissolve in concentrated sulphuric acid, forming a deep purple or violet solution; in the case of nitroamino-2:4-dichlorobenzene, which has an *o*-hydrogen atom, addition of water immediately destroys the purple colour, and a yellow precipitate of 2:4-dichloro-6-nitroaniline is formed; in the case of the other nitroamines, in which the hydrogen atoms in positions 2, 4, and 6 are replaced by other atoms or groups, water precipitates from the purple solution a red solid; the latter contains among other substances a di-*o*-substituted β -nitroaniline if the original nitroamine had a β -bromine atom. The purple solutions in sulphuric acid may possibly correspond to an intermediate stage between the nitroamine and the nitrated aniline.

*72. "The Atomic Weight of Tellurium." Preliminary notice. By A. SCOTT.

The many attempts to determine the atomic weight of tellurium which have been published since Mendeleeff published his well-known table of elements, indicate very clearly the general recognition that experimental results did not sanction the assignment of a lower atomic weight to tellurium than that of iodine. The problem was rendered more complicated by the variations in the

numbers obtained by the same experimenter when he employed different methods in his determinations. This gave rise to the suspicion that the substance purified by the best methods was, or at least might be, a mixture of the true tellurium with a higher homologue. All the most recent researches, and especially those of Pellini (*Ber.*, 1901, xxiv., 3807) and of Köthner (*Annalen*, 1901, ccix., 1), seem conclusively to prove, however, that the atomic weight of tellurium is very near 127.64, that of iodine being 126.85. For more than a year the author has been at work on this subject, and his results are entirely in agreement with those of the above-mentioned experimenters. It was obvious that the most satisfactory substance for such determinations should contain both tellurium and iodine, and be weighted with as little as possible of other elements. Such a substance is trimethyl tellurium iodide, which is easily prepared and purified, is very stable, and non-hygroscopic. When tellurium is heated to 80–100° in a sealed tube with methyl iodide (Demarçay, *Bull. Soc. Chim.*, 1883, xl., 100), dimethyl tellurium di-iodide is readily formed; when this is treated with reducing agents in presence of methyl iodide, trimethyl tellurium iodide, $\text{Te}(\text{CH}_3)_3\text{I}$, is readily obtained. The corresponding bromide is a salt very well adapted for titration with silver by the method of Stas. Preliminary determinations so far agree with all the best results hitherto published in proving that the atomic weight of tellurium is nearly a unit higher than that of iodine.

In the following determinations, all the weights given are corrected for errors in face values of the weights, as well as being brought to vacuum standards:—

$\text{Te}(\text{CH}_3)_3\text{I}$. AgI.
1.7461 gave 1.3688 $\therefore \text{Te}(\text{CH}_3)_3\text{I} = 299.62$ and $\text{Te} = 127.70$.
6.6425 " 5.20575 $\therefore \text{Te}(\text{CH}_3)_3\text{I} = 299.58$ " $\text{Te} = 127.66$.
8.0628 " 6.3181 $\therefore \text{Te}(\text{CH}_3)_3\text{I} = 299.61$ " $\text{Te} = 127.69$.

By titration:—

2.4294 $\text{Te}(\text{CH}_3)_3\text{Br}$ required 1.0373 Ag $\therefore \text{Te}(\text{CH}_3)_3\text{Br} = 252.79$ and $\text{Te} = 127.77$.
6.8424 $\text{Te}(\text{CH}_3)_3\text{Br}$ required 2.9201 Ag $\therefore \text{Te}(\text{CH}_3)_3\text{Br} = 252.90$ and $\text{Te} = 127.88$.

The second sample of bromide was not so pure as the first, as it was the second crop of crystals obtained from the mother-liquors. The mean value is therefore $\text{Te} = 127.74$ taking all five determinations, or 127.70 if only the first four be taken.

Pellini gives 127.64.

Köthner " 127.63.

The author indicated by a graphic representation of the quotients—

$$\frac{\text{F}}{\text{O}} = 1.190, \frac{\text{Cl}}{\text{S}} = 1.105, \frac{\text{Br}}{\text{Se}} = 1.009, \frac{\text{I}}{\text{Te}} = 0.993,$$

obtained by dividing the atomic weights of the halogen elements by those of the corresponding members of the oxygen group respectively, why he thought it very unlikely that the atomic weight of iodine should exceed that of tellurium.

In making the necessary calculations, the following values were taken:—C=12.00; H=1.0075; I=126.85; Br=79.95 (O=16).

Two syntheses of silver iodide were made, as follows:—

Ag. AgI.
4.6240 gave 10.0634 $\therefore \text{AgI} = 234.89$ and $\text{I} = 126.96$
6.39978 " 13.92913 $\therefore \text{AgI} = 234.91$ " $\text{I} = 126.98$

Substituting $\text{I} = 126.97$ for $\text{I} = 126.85$ in the first three calculations increases the values for $\text{Te}(\text{CH}_3)_3\text{I}$ by 0.15, and those for Te by 0.03.

73. "Nitrogen Bromides containing the Propionyl Group." By F. D. CHATTAWAY.

Propionanilide and the bromopropionanilides readily react with hypobromous acid, the imino-hydrogen being replaced by bromine, a hypobromite being probably formed as an intermediate product.

The action is a reversible one, and when nitrogen

bromides are placed in water the opposite change takes place until a position of equilibrium is reached.

Except in colour, these nitrogen bromides closely resemble the corresponding nitrogen chlorides. All show the characteristic behaviour of the nitrogen halogen linkage, and readily react with hydriodic acid, sulphurous acid, hydrogen sulphide, alcohol, and potassium cyanide.

When an unsubstituted or partially substituted phenyl residue is attached to the nitrogen, they very readily undergo isomeric change.

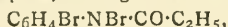
Interchange between bromine attached to the nitrogen and hydrogen in the ortho-position in an unsubstituted nucleus has not been observed. Apparently the halogen cannot pass from the nitrogen to a meta-position.

All nitrogen bromides, when treated with an excess of hydrobromic acid, are decomposed, bromine being liberated and the corresponding anilide re-formed. On the other hand, when an anilide is treated with an excess of bromine, a nitrogen bromide and hydrobromic acid are produced.

A large excess of hydrobromic acid or the continuous removal of the free bromine causes the anilide to be re-formed, whilst the addition of a salt of a weaker acid which can remove the hydrobromic acid causes the action to proceed in the opposite direction, and a nitrogen bromide is produced. The reversible nature of this reaction is most clearly seen when the nucleus is already fully substituted, as otherwise isomeric change and substitution into the ring may take place.

The following substances have been prepared:—

Propionylphenyl nitrogen bromide, $C_6H_5 \cdot NBr \cdot CO \cdot C_2H_5$, pale yellow pyramids, m. p. 88° ; *p-bromopropionanilide*, $C_6H_4Br \cdot NH \cdot CO \cdot C_2H_5$, rectangular plates, m. p. 149° ; *propionyl-p-bromophenyl nitrogen bromide*, $C_6H_4Br \cdot NBr \cdot CO \cdot C_2H_5$, yellow prisms, m. p. 78° ; *propionyl-p-bromophenyl nitrogen chloride*, $C_6H_4Br \cdot NCl \cdot CO \cdot C_2H_5$, colourless plates, m. p. 59° ; *o-bromopropionanilide*, $C_6H_4Br \cdot NH \cdot CO \cdot C_2H_5$, colourless prisms, m. p. 93° ; *propionyl-o-bromophenyl nitrogen bromide*,—



yellow prisms, m. p. 117° ; *propionyl-o-bromophenyl nitrogen chloride*, $C_6H_4Br \cdot NCl \cdot CO \cdot C_2H_5$, colourless rhombs, m. p. 59° ; *2:4-dibromopropionanilide*, $C_6H_3Br_2 \cdot NH \cdot CO \cdot C_2H_5$, colourless needles, m. p. 136° ; *propionyl 2:4-dibromophenyl nitrogen bromide*, $C_6H_3Br_2 \cdot NBr \cdot CO \cdot C_2H_5$, yellow rhombs, m. p. 87° ; *propionyl 2:4-dibromophenyl nitrogen chloride*, $C_6H_3Br_2 \cdot NCl \cdot CO \cdot C_2H_5$, colourless plates, m. p. 71° ; *2:4:6-tribromopropionanilide*, $C_6H_2Br_3 \cdot NH \cdot CO \cdot C_2H_5$, colourless prisms, m. p. 203° ; *propionyl 2:4:6-tribromophenyl nitrogen bromide*, $C_6H_2Br_3 \cdot NBr \cdot CO \cdot C_2H_5$, yellow prisms, m. p. 82° ; *propionyl 2:4:6-tribromophenyl nitrogen chloride*, $C_6H_2Br_3 \cdot NCl \cdot CO \cdot C_2H_5$, colourless prisms, m. p. 75° .

THE ROYAL SOCIETY.

CONVERSAZIONE AT BURLINGTON HOUSE.

ON Wednesday evening last (May 14, 1902) a Conversazione was held at the Society's Rooms, at Burlington House, and was largely attended by the Fellows and their guests.

The visitors were received by the President, Sir William Huggins, K.C.B., D.C.L., and the members of the Council.

Among the numerous and interesting exhibits, we may mention an improved form of Thomson Coal Calorimeter, exhibited by Mr. W. ROSENHAIN, in which the combustion chamber is specially designed to give easy manipulation, complete combustion, and complete transference of the heat of combustion to the water of the calorimeter. A special system of valves secures the thorough cooling of all escaping gases, by washing out the interior of the combustion chamber with the water of the calorimeter at the end of the combustion.

Mr. J. MACKENZIE-DAVIDSON exhibited some Stereoscopic X-Ray Transparencies and Negatives, two X-Ray Photographs of a bullet fired from a revolver, and, during the evening, showed the Development of Photographic Negatives in Ordinary Light, by which a reversed negative is obtained.

The Badische Anilin und Soda-Fabrik had an exhibit of Synthetic Indigo; they comprised—

(a) Specimens of the raw material (naphthalene) and the intermediate products formed in the manufacture of synthetic indigo, as well as of the latter in four different forms.

(b) Examples of various textile materials illustrating the application of synthetic indigo on loose wool, slubbing, military cloths of different nations, cops, cross-reeled bundles, cotton piece goods, both dyed and printed.

The initial material is naphthalene; this is converted by oxidation with sulphuric acid into phthalic anhydride, and the latter is next transformed into anthranilic acid, which, in conjunction with chloracetic acid, yields phenylglycin-ortho-carboxylic acid. The latter body is treated with a caustic alkali at a high temperature, and yields indoxyl or indoxyllic acid.

It is interesting to note that this product indoxyl also results in the treatment of the indigo plant as practised in the tropics.

The last stage in the process, whether starting from naphthalene or from the indigo plant, is identical, viz., the oxidation of indoxyl into indigo.

An Apparatus for Natural Colour Photography, and examples of its applications, were shown by Messrs. SANGER, SHEPHERD, and Co. This process of natural colour photography is based upon Young's theory of trichromatic vision. Negatives or colour records of the object are taken through colour filters admitting light of the three primary sensations—red, green, and blue-violet—in accordance with the power of the respective sensations to excite the eye. From the three negatives three coloured positives are printed upon a special film, which, when mounted in superposition, exactly reproduce the form and colour of the object photographed.

There were also—

A New Camera for securing the three negatives through one lens at one exposure, and

A Camera for Photomicrographic Work fitted with colour filters for Natural Colour Photography.

Prof. H. A. MIERS exhibited some Attempts to reproduce Polarisation Effects by Three-colour Printing. These are collotype prints from photographs of the coloured interference figures produced by crystal sections in a polariscope. The most successful of the reproductions is that of the figure yielded by a crystal of orthoclase felspar. The differences in the rings of the three monochromatic prints are in this case very noticeable.

Some Experiments illustrating the Effect of Ultra-Violet Light on the Electric Discharge were shown by Prof. J. A. FLEMING. The effect of ultra-violet light in promoting electric discharge was discovered by Hertz in 1887 and has been much investigated since. The experiments exhibited show the action of the ultra-violet light emitted from the edge of the coating of a Leyden jar upon the spark of an induction coil charging it. The jar is arranged between two spark gaps in parallel, one larger than the other and both connected to the terminals of an induction coil. The jar is placed nearest to the shorter gap. The spark then happens always at the shorter gap. If a plate of glass or mica, both of which are very opaque to ultra-violet light, is then interposed between the jar and the active gap, a spark at once appears at the other gap. This spark can be quenched by illuminating the first or shorter gap with ultra-violet light from burning magnesium or a naked electric arc, and this can be done from considerable distances.

Dr. DAWSON TURNER also showed some Effects of Ultra-

Violet Radiation. Rock-salt appears to be the most transparent substance to this particular radiation.

Mr. W. R. PIDGEON exhibited a New Electrical Influence Machine suitable for Campaign Work. The sectors are imbedded in "violetite," and there is no glass or wax used in the machine, so that it will resist hard usage, even abuse, and when mounted on an iron frame is suitable for X-ray work in camp, or for work in India, and other countries, where the heat makes it difficult to preserve induction coils.

Prof. W. RAMSAY showed a Krypton Tube. Many persons see the colour of a vacuum tube containing krypton as lilac, many as green. The phenomenon appears to be conditioned by the size of the yellow spot on the retina.

A very simple Electricity Meter was shown by Messrs. G. L. FRICKER and W. MORDEY. It is suitable for both direct and alternating currents; is unaffected by changes of periodicity, and only requires to be wound once every three months or so.

Dr. A. MUIRHEAD gave a demonstration of Re-transmission on Submarine Telegraph Cables. In the cable relay the local contacts are made between a metallic arm, which is connected by fibres to the signal coil, and a metallic body whose surface is divided by their insulating partitions into three sections, to constitute the two terminals of a local line or re-transmitting battery, with a zero section between.

Two demonstrations, by means of the Electric Lantern, were given in the Meeting Hall: one at 9.45 p.m., by Sir H. TRUEMAN WOOD on the Application of Photography to the production of Pictures in Colour; and one at 10.45 p.m., by Dr. R. D. ROBERTS, who showed a number of Lantern Slides in Natural Colours, of the Grand Cañon of the Colorado, the Sierra Nevada, California, and the Yellowstone Park.

PHYSICAL SOCIETY.

Ordinary Meeting, May 9th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

Dr. P. E. SHAW exhibited a Simple Electric Micrometer.

Two years ago Dr. Shaw described an instrument with which he measured very small lengths by the application of electric contacts, and the micrometer shown was a simple form of the original apparatus. A screw, fitted with a milled head, turns in a fixed nut, and its lower end presses upon the extremity of the long arm of a lever. A metal point is attached to the short arm, and the distance through which it moves, on turning the milled head, can be deduced from a knowledge of the pitch of the screw, and the ratio between the arms of the lever. In using the instrument this point is always brought up to a metal surface, and the contact is accurately determined by the telephonic arrangement described in connection with the original micrometer. Dr. Shaw illustrated the use of the instrument for measuring small lengths by describing the following eight applications to ordinary laboratory measurements:—(1). The measurement of the thickness of plates, films, or fibres. The object is placed between two metal plates. The point of the micrometer is adjusted to touch the top plate, and the reading taken. The object is removed, the point is again brought into contact with the top plate, and the difference between the readings in the two cases gives the thickness of the film. (2). The determination of Young's modulus by the elongation of a wire. Dr. Shaw described experiments on two wires, each $2\frac{1}{2}$ metres long, hanging side by side, one of copper and the other of steel. The wires terminated in horizontal platforms to which the stretching weights were attached. The base of the instrument rested on one platform, while depressions of the other, due to loading, were measured.

In this way any error, on account of the bending of the beam from which the wires were hung, was eliminated. (3). The determination of Young's modulus by the bending of a beam. (4). The determination of simple rigidity by a static method. Observations were made upon a rod held horizontally by rigid wall brackets. One end of the rod was fixed, and the other held in position by a pin pressed into a hole in the end of the rod. From this end an arm projected outwards. Weights were applied to the extremity of this arm, and the twist measured by observing with the micrometer the movement of the end of the arm. (5). Application to the extensometer. (6). Measurement of thermal expansion. (7). Microscopic measurements. In measuring the diameter of a capillary tube the cross-wire of the microscope is made to touch one side of the tube, and the point of the micrometer is brought into contact with the metal stage. The stage is then moved by a screw until the cross-wire comes to the other side of the tube. The micrometer point is moved into contact again, and the difference in the readings gives the diameter of the tube. In this measurement the full magnifying power of the microscope is utilised, and the work of moving the stage is performed by a rough screw. (8). The direct measurement of the wave-length of light. Newton's rings are formed by a convex lens and a piece of plate-glass. The convex lens is fixed to the short arm of the lever, and the distance through which it must be moved to cause a certain number of bands to appear at the centre gives a means of calculating the wave-length of the light employed.

Prof. EVERETT said the apparatus combined fineness and accuracy of measurement, and expressed his interest in the determination of distances with the microscope.

Mr. R. J. SOWTER asked if any special precautions had been taken to prevent deformation in the instrument. If not, then it was optimistic to assume that one or more multiplying levers could be used to measure lengths of the order of a millionth of a m.m. with any physical accuracy, assuming the multiplication of measurement to be according to the law of the lever as Dr. Shaw apparently did.

Mr. W. WATSON said that in determining the wave-length of light by Newton's rings it was necessary to measure from the knife-edge of the lever to the centre of the rings. The accuracy of the experiment was limited by the difficulty in judging the centre. The variation of the temperature of the air would distort the lever, and produce errors. In reference to the experiments on Young's modulus, using two wires of different material, he said that no precautions had been taken to procure a steady temperature, and pointed out that variations in temperature would affect the two wires unequally. In the experiment on the torsion of a rod the twisting had been produced by an unbalanced force. The other arm of the necessary couple must therefore have been unsatisfactorily supplied by the friction of the pin which held the rod in position. In measuring the diameter of a capillary tube with extreme accuracy it was necessary to have a normal section, which was somewhat difficult to obtain. Dr. Shaw apparently considered the instrument suitable for laboratory work. If it was for students it was unnecessarily elaborate, and if for obtaining accurate measurements there were objections and uncertainties which should be investigated. Mr. Watson said that a similar form of micrometer had been described by Mr. H. C. Russell, and used in the observatory at Sydney.

Mr. J. M. BARR said that as errors would be introduced by variations in temperature, it might be advisable to make the instrument of a nickel steel alloy with a small coefficient of expansion. He asked if the knife-edges and screws used were good enough to give the same reading twice, and said he thought the limit of physical accuracy could be obtained by using a single disc on a screw calibrated throughout its length. He considered one ten-thousandth of an inch to be about the limit attainable by such methods.

Dr. SHAW, in reply, said the main justification of the

apparatus was in the consistency of the results given by it; these were excellent, as the tables given in the paper showed. The method had been shown to be much more accurate than those in general use. As to the contention that the apparatus, while too sensitive for laboratory practice, was not sufficiently so for research on length changes, he pointed out that the accuracy of all measuring instruments was always on the increase, so that laboratory methods which were considered good recently would not necessarily suffice in the immediate future. Why be content, even for teaching students, with measuring to the one-fiftieth of a millimetre by the microscope when with the simple electric micrometer we get, with little trouble, to the thousandth of a millimetre? Dr. Shaw knew nothing of the prior publication in Australia mentioned by Mr. Watson; if there were such a method introduced years ago it was all the more astounding that Mr. Russell and his successors should have allowed such an excellent idea to lapse and remain immature and unknown. Some speakers had suggested that uncertain deformation of the levers might occur during an experiment and vitiate results; but a new strain implied a new stress, and unless a definite change occurred in the forces of the system we could not suppose a change in deformation. A like answer was given to the criticism that the levers might expand under heat during a measurement. Why if sufficient time has elapsed to allow the system to attain temperature equilibrium should anyone postulate expansions without indicating a new or irregular source of heat? Most of the above supposed evils of course existed, but they were of small account. As with every good apparatus ever produced, if ordinary and suitable precautions be taken, these errors were reduced to a lower order of importance, and could be neglected. In conclusion, the method had been firmly established in University College, Nottingham, and had superseded other apparatus. It would no doubt spread and become general.

Papers on "*The Conservation of Entropy*," by Mr. J. A. ERSKINE, and "*Rational Units of Electromagnetism*," by Signor G. GIORGI, were postponed; and the Society adjourned until May 23, 1902.

NOTICES OF BOOKS.

The New Volumes of the Encyclopædia Britannica. Constituting the Tenth Edition of that Work. The First of the New Volumes being Vol. XXV. of the Complete Work. London: *The Times*. Edinburgh: A. and C. Black. 1902. Pp. 808.

WHILST of considerable general interest a work such as this does not alone appeal to chemists and physicists, but equally to all groups of scientific men. This volume only extends to the end of the letter "A," and thus cannot comprise any great number of chemical subjects: we find a short article on Alloys, by Sir Wm. Roberts-Austen; one on Acetylene, by Vivian B. Lewes; Adulteration, by Otto Hehner; Aluminium, by E. Ristori; Aether, by J. Larmor; Argon, by Lord Rayleigh; and Assaying, by A. Blair. Each of these subjects is treated in the efficient manner we should expect considering the reputations of the experts who have undertaken the articles, and if the other branches of knowledge are dealt with in the same manner (and there is every evidence that this will be the case) we feel sure that these new volumes will ample fulfil the expectations of their publishers.

The Gas Engineer's Laboratory Handbook. By JOHN HORNBY, F.I.C. Second Edition, Revised and Enlarged. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1902. Pp. 312.

In revising this book it would have been as well if the author had entirely omitted the first thirty-nine pages

which form Part I. The information given in this part is so thoroughly elementary that we can hardly conceive any gas engineer troubling to do more than glance at the pages and pass on. The very idea of explaining to the chemist at a gas works the difference between "qualitative" and "quantitative" analysis is absurd; the same may be said of the information given on pages 24 and 25, where the chemist is shown how to fold a filter-paper, and how to pour a solution out of a beaker into a funnel with the help of a glass rod; these instructions, by-the-by, include three illustrations. Fig. 14 illustrates a "wash-bottle," and a very bad one at that; while on page 34 we find a picture of a pipe-clay triangle. What could be more unnecessary than to include such matter, which the veriest tyro should have at his finger ends?

The really useful portion of this book is in Part IV., on special analysis required in gas-works, and Part V., on technical gas analysis, calorimetry, estimation of cyanogen in gas, and the valuation of oils for gas-making purposes. Additional chapters have been added to the section on gas analysis; these include the description and use of the Orsat-Muencke apparatus, the method of determining the calorific power of gas, &c. This latter is of importance from the fact that heating by gas is coming more and more into general use.

The Orsat-Muencke apparatus is extremely useful for performing the technical gas analysis required in gas-works; it is applicable for the estimation of the absorbable constituents of such gaseous mixtures as crude coal-gas, water-gas, furnace and chimney-gases, &c. The apparatus is fully described and illustrated on pages 240—244.

In the appendix, which follows Part V., the Gas Referees' Instructions are given as to the times and mode of testing for purity, together with the useful and necessary tables for simplifying the calculation of results. The book is well indexed, and has a full table of contents.

Subject List of Works on Certain Chemical Industries in the Library of the Patent Office. London: Darling and Son, Ltd., and The Patent Office. 1901. Pp. 100.

THIS list, which is of undoubted value, is similar in form to the one already noticed (*CHEMICAL NEWS*, vol. lxxxv., p. 23), and unites under one cover the literature of certain organic industries usually associated in chemical literature. These subjects are divided naturally into five groups:—(1) Destructive Distillation Industries, including systems of lighting with hydrocarbons; (2) Industries of the Oils and Fats, viz., soap, perfumery, lubricants, candles, paints, and varnishes; (3) Industries of the Gums and Resins, including indiarubber and waterproofing; (4) Paper-making; and (5) Leather Manufacture. The present list comprises 1003 works representing some 1990 volumes, which are distributed under 151 headings and sub-headings.

The Electric Arc. By HERTHA AYRTON, M.I.E.E. London: *The Electrician* Printing and Publishing Co., Ltd. Pp. 479.

IN experimenting on the arc, the author's aim has been not so much to add to the large number of isolated facts already known, as to form some idea of the bearing these facts have one on the other. The attempt to correlate all the known phenomena, and to bind them together into one consistent whole, led to the deduction of new ideas which, when tested, became parts of the growing body of facts; in this manner the subject has grown and developed until it has reached its present magnitude and importance.

The theory which is presented in Chapter XII. has not been hastily built up to fit a few of the more salient characteristics of the arc, but has literally evolved itself during the course of a detailed study of each separate phenomenon. The central idea of this theory, that the carbon vapour changed into mist at a short distance from the crater dates from an early period of the author's work,

while the full recognition of all it entailed has followed slowly as each part of the subject was considered in turn.

The book is divided into twelve chapters, and contains 146 illustrations and 58 tables. The early chapters deal with the appearance and history of the arc, and the technical part of the work begins in Chapter III., on "striking" the arc, and sudden variations of current.

From Chapter IV. to Chapter IX. we have to do with current, electromotive force, potential difference between the carbons, &c., in all their varying bearings on the arc, its formation, behaviour, &c.

Chapter X. is on "hissing arcs," a subject which the author has made particularly her own, though much excellent work on this subject has been done by Trotter, Duddell, and others.

Chapter XI., which is an important one, is devoted to the consideration of the light and luminous efficiency of the arc; while Chapter XII., and last, on the mechanism of the arc, consists principally of matter embodied in a paper read before the Royal Society, June 20, 1901, on this subject.

This volume is a standing record of long and patient investigations, not of hurriedly put forward ideas, and shows careful weighing of all the evidence. At the end of each chapter there is a summary of the matter that has just been considered, wherein the author's conclusions are plainly and concisely set forth. The book is well and clearly printed, and the table of contents and index are satisfactory, while the short list of errata does not contain any correction of great moment; there is, however, one oversight to which we may draw attention: Chapter I. commences with the words, "Since the discovery of the electric arc early in the present century"; obviously a slip, which does not at all affect the high character of the book.

CORRESPONDENCE.

ARSENITE OF SILVER.

To the Editor of the Chemical News.

SIR,—I have read the curious letter signed A. G. Bloxam, which only becomes intelligible on the assumption that the writer of it was unacquainted with the contents of the admirable paper published by Bloxam in the *Journal of the Chemical Society* in the year 1862. One of the most interesting results published in that paper is the investigation of the zinc-salt of arsenious acid, the nature of which was made out in the most satisfactory manner. There are great difficulties in investigating the salts of such an acid as arsenious acid, and it reflects no discredit on Bloxam that he was not so fortunate with the silver-salt as with the zinc-salt.—I am, &c.,

J. ALFRED WANKLYN.

The Laboratory, New Malden, Surrey,
May 11, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

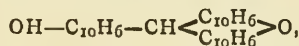
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiv., No. 16, April 21, 1902.

Certain Phenomena of Voltaic Polarisation.—M. Berthelot.—Whilst examining voltaic action resulting from the reciprocal action of two liquids, phenomena of polarisation are often observed. These the author investigates, and especially the action of formic acid in such a case.

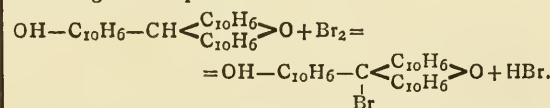
Absorption of Radio-activity by Liquids.—T. Tommasina.—Continuing his researches on the nature of the electric modification produced by radio-activity and the rapidity of appearance and disappearance of the phenomena in air, which happens almost immediately at the time of its maximum intensity, the author establishes the fact that the conductivity of liquid and solid dielectrics seems to increase under the action of radio-activity. The study of the absorption of the radio-activity is examined quantitatively, the substances experimented with being—carbon disulphide, toluol, benzene, essence of terebenthine, alcohol, oil of vaseline, petrol, distilled water, Rhone water, ammonia, concentrated solution of sodium bicarbonate, 10 per cent solution of sulphuric acid, 2 per cent solution of copper sulphate, acetic acid, lead acetate, amyl acetate, glycerin.

Formation of Negative Images under the Action of certain Vapours.—P. Vignon.—M. Colson's experiments in 1896 showed that zinc at ordinary temperatures emits vapours capable of altering photographic plates in the dark. Russell's experiments tend to the same result. The author now succeeds in obtaining images of medals dusted over with powdered zinc. These images are the negatives, not formed by the intervention of light and shadows, since they operate in total darkness. He also succeeds in obtaining negative images by allowing ammoniacal vapours to act on linen impregnated with a mixture obtained by grinding together powdered aloes and olive oil.

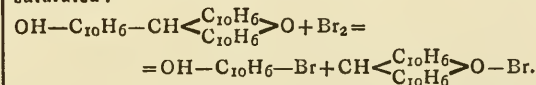
A Case of Molecular Rupture by means of Bromine.—R. Fosse.—The author hoped to obtain by the action of bromine on naphtholdinaphthoxanthene,—



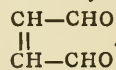
hydrobromic ether of naphtholdinaphthoxanthidrol formed according to the equation—



He finds, however, that HBr is not produced, but the bromine is fixed on to the molecule as if it were not saturated:—



Certain Derivatives of Fumaric Dialdehyde.—R. Marquis.—Acetine of nitrosuccinic aldehyde, described in a preceding paper, is decomposed by hot water at 80° into acetic acid, nitrous acid, and another product of aldehydic nature which remains dissolved in the water. Several derivatives of this product are prepared, its oxime and the benzoyl derivative of this, which his researches lead him to believe is a dialdehyde, and of constitution—



Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxv., Nos. 20—21.

Sulphuric and Disulphuric Anhydrides.—G. Oddo.—Already inserted in full.

Acidimetry of Phosphoric Acid by means of the Alkaline Earths.—J. Cavalier.—Already noticed.

Oxidation of Propylglycol by means of the Oxidising Ferments.—André Kling.—Already noticed.

Action of Reducing Agents on the Two Isomeric Nitrodimethylacrylates of Ethyl.—L. Bouveault and A. Wahl.—Already noticed.

Nitroacetate of Ethyl.—A. Wahl.—Already noticed.

Action of Alcoholic Ammonia on the *o*-Bromised Derivatives of Methyl-*p*-chlorophenylketone and Methyl-*p*-bromophenylketone.—A. Collet.—Twenty grms. of bromomethyl-*p*-chlorophenylketone were added to an excess (about 200 c.c.) of alcohol at 93° saturated with ammonia gas at the ordinary temperature; after being well shaken this is left to stand. The temperature rises slightly, and the liquid soon becomes of a golden-yellow colour. On the following day it deposits a reddish crystalline mass, which is collected on a filter and washed with cold water to eliminate the bromide of ammonium it may contain. In this manner about 6 or 7 grms. of a substance are obtained, which is purified by crystallisation in boiling acetic acid, forming yellowish crystals, which are transformed into almost colourless plates by a fresh crystallisation in chloroform. This substance has the composition of a di-*p*-chlorophenyl- γ -diazine, and its formula is $C_4H_2N_2(C_6H_4Cl)_2$; it is fusible at 200–201°, slightly soluble in boiling alcohol, more so in acetic acid, but especially so in chloroform. Bromomethyl-*p*-bromophenylketone, treated with alcoholic ammonia under the same conditions, gives a strongly coloured, deep reddish-brown liquid, which, after twenty-four hours, deposits a bright red crystalline mass (about 9 or 10 grms.). This deposit is purified by crystallisation in chloroform. It is di-*p*-bromophenyl- γ -diazine, $C_4H_2N_2(C_6H_4Br)_2$, fusible at 235–236°, slightly soluble in boiling alcohol and acetic acid and more so in chloroform. Both these diazines are soluble in boiling nitric acid (sp. gr. 1.40) and are deposited unchanged on cooling.

Pipette for the Determination of the Density of Liquids.—F. Girardet.—This paper requires the accompanying diagram.

MISCELLANEOUS.

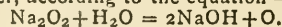
The Royal Society.—The following are the fifteen selected candidates for election:—H. Brereton Baker, Prof. Henry T. Bovey, Prof. Rupert Boyce, John Brown, William Bate Hardy, Alfred Harker, Sydney S. Hough, Robert Kidston, Thomas Mather, John Henry Michell, Hugh Frank Newall, Prof. W. M. Flinders Petrie, William Jackson Pope, Edward Saunders, Dr. Arthur Willey.

Royal Institution.—On Tuesday next, May 20th, at three o'clock, Professor Karl Pearson will deliver the first of three lectures at the Royal Institution on "The Laws of Heredity, with special reference to Man"; and on Thursday, May 22nd, Mr. M. H. Spielmann commences a course of three lectures on "Contemporary British Sculpture," with lantern slide illustrations; and on Saturday, May 24th, Professor Brander Matthews begins a course of three lectures on "The Development of the British Drama." The Friday Evening Discourse on May 23rd will be given by Canon Ainger, his subject being "The Ethical Element in Shakespeare"; the Discourse on May 30th will be delivered by Mr. G. Marconi on "Electric Space Telegraphy"; and that on June 6th by Sir Benjamin Baker on the "Nile Reservoirs and Dams."

School Board for London.—Annual Exhibition of Handwork.—The Annual Exhibition of work executed in the Board Schools of London will be held at the Examination Hall, Victoria Embankment, W.C. (adjoining Waterloo Bridge), on Wednesday, June 18th, 1902, and the three following days. The Exhibition will be opened by Lord Reay, G.C.S.I., G.C.I.E. (Chairman of the Board), at 3 o'clock p.m., and will include specimens of Drawings, Colourwork, Modelling, Woodwork, Woodcarving, Metalwork, Needlework, Infants' work, Cookery, Laundrywork, Housewifery from the Day and Evening Schools, work from the Schools for the Blind, Deaf and Special Instruction, and also work from the Truant and Industrial Schools. There will also be included Scientific Apparatus which

has been constructed by the teachers and pupils. The Exhibition this year should prove of particular interest, and it is hoped, inasmuch as admission to it will be entirely free, that the people of London will take this opportunity of seeing the really marvellous results obtained.

Oxylith.—The recent invention of "oxylith," due to M. Jaubert, will help to make the use of nascent oxygen still more wide in its applications. It consists of agglomerated peroxide of sodium which contains 15 litres of chemically pure oxygen (99.9 per cent) in every 100 grms. This oxygen is given off on placing the "oxylith" in contact with water, according to the equation—



An automatic generator, simple in its action, can be obtained so that a supply of pure oxygen can always be kept at hand in places where it is likely to be wanted suddenly. In certain severe illnesses, collapse after surgical operations, in cases of strangulation, suffocation, and inhalation of noxious gases requiring immediate treatment, the oxygen generator will be found invaluable. It has also been used in submarine boats, to supply "artificial air," the caustic soda formed being at the same time used for absorbing the carbonic acid.

MEETINGS FOR THE WEEK.

TUESDAY, 20th.—Royal Institution, 3. "The Laws of Heredity, with special reference to Man," by Prof. Karl Pearson, M.A., F.R.S.

WEDNESDAY, 21st.—Microscopical, 7.30. Exhibition of Freshwater Entomostraca, by D. J. Scourfield.

THURSDAY, 22nd.—Royal Institution, 3. "Contemporary British Sculpture," by M. H. Spielmann.

FRIDAY, 23rd.—Royal Institution, 9. "The Ethical Element in Shakespeare," by The Rev. Canon Ainger, M.A., LL.D.

Physical, 5.

SATURDAY, 24th.—Royal Institution, 3. "The Development of the English Drama—I, The Art of the Dramatist," by Prof. Brander Matthews, Litt.D., D.C.L.

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THE CHEMICAL NEWS.

VOL. LXXXV., No. 2217.

THE CONDITIONS DETERMINATIVE OF CHEMICAL CHANGE AND OF ELECTRICAL CONDUCTION IN GASES, AND ON THE PHENOMENA OF LUMINOSITY.*

By HENRY E. ARMSTRONG, V.P.R.S.

IN his communication to the Chemical Society on the union of oxygen and hydrogen, read at the meeting on February 19 (*Chem. Soc. Proc.*, 1902, 40), Mr. H. Brereton Baker has added another to his brilliant series of proofs that interactions supposed to take place between two substances are in reality of a more complex character; and having successfully demonstrated, in the case of the gases referred to, that water alone does not determine the interaction, he has, I believe, carried the investigation to the final stage which it was essential it should reach to make it a complete discovery of the nature of the process.

Mr. Baker has shown that when a mixture of hydrogen and oxygen [most carefully prepared by electrolysis of a solution of barium hydrate] is enclosed in a chamber of hard Jena glass [cleansed in the most careful manner possible], and the mixture is dried as thoroughly as may be [by means of phosphoric anhydride which has been carefully purified by distilling it in a current of air], no appreciable interaction takes place between the gases, even on heating the tube to redness. If the drying be not carried too far, however, water is gradually but very slowly formed—finally in sufficient quantity to be visible; and yet, even when water is visibly present, no explosion takes place.

The interpretation I would give of these observations is as follows:—The amount of *impurity* present in the gases being reduced to a minimum, *i.e.*, the gases being almost dry and almost free from impurities *which in admixture with water constitute a conducting system*, change takes place at a very slow rate when heat is applied; and even when a considerable amount of water is present, the amount of associated impurity is too small to raise the conductivity—the rate of formation of conducting systems—to a point at which the rate of change would be such as to give rise to an explosive wave.

As defining the conditions which it has long been my opinion are necessary to the occurrence of chemical change in gases and generally, I may refer to words used by me in 1893.

("Eight years ago, in the course of the discussion on Mr. H. B. Baker's communication on "Combustion in Dried Gases" (*Roy. Soc. Proc.*, 1885, 40), I defined chemical action as *reversed electrolysis*; in other words, in order that chemical action may take place, it is essential that the system operated on comprise an electrolyte. I then pointed out that as neither hydrogen nor oxygen was an electrolyte, a mixture of only these two gases should not be explosive; and, moreover, that as water was not an electrolyte, and it was scarcely probable that water and [either] oxygen or hydrogen would form an electrolyte, it was difficult to understand how the presence of water pure and simple should be of influence in the case of a mixture of hydrogen and oxygen. This forecast has since been verified, the remarkable series of experiments carried out by V. Meyer in conjunction with Krause and Askenasy having clearly demonstrated that the formation of water from hydrogen and oxygen takes place at an irregular rate, and is, there-

fore, dependent on the presence of a something other than water—I imagine an acid impurity. But this is a consideration which has not yet received the proper attention, and it is, therefore, desirable to emphasise its importance by reference to other cases. Mr. Baker's recent preliminary note on the influence of moisture in promoting chemical action (*ante*, p. 229) affords several interesting examples:—Thus, he states that neither does hydrogen chloride combine with ammonia nor is nitric oxide oxidised by oxygen if moisture be excluded. In the former case, the addition of water should suffice to determine the combination, as water and hydrogen chloride together form a 'composite electrolyte' (*cf. Roy. Soc. Proc.*, 1886, No. 243, p. 268); as neither nitric oxide nor oxygen, however, forms a composite electrolyte with water, in this case water alone should not determine the occurrence of change—but if by the introduction of a trace of 'impurity' in addition to water the presence of a composite electrolyte were secured (however high its resistance, owing to the smallness of the amount of 'impurity'), action would set in, and when once commenced would proceed at an increasing rate, as nitric acid would be formed, and the resistance of the electrolyte would consequently diminish. On this account it will be a task of exceeding difficulty to demonstrate experimentally that nitric oxide and oxygen are inactive in presence of water alone; but there can be no doubt that such must eventually be admitted to be the case, provided always that it is permissible to extrapolate Kohlrausch's observations, and to conclude from them that *pure water is a dielectric*."—*Chem. Soc. Proc.*, 1893, 145).

I venture to call attention to them, not because I have any particular wish to put forward a claim on my own behalf, but in the hope of attracting attention to a subject of surpassing importance, which both chemists and physicists have hitherto most strangely neglected to consider *in all its bearings*.

[In his complete paper (*Chem. Soc. Trans.*, 1902, p. 400), Mr. Baker states that he found that hydrogen and oxygen did not interact when subjected to the influence of a coil of thin silver wire, heated by an electric current to the melting-point of the silver, that is to say, above 1000°; but that when a similar platinum coil was tested in the dried gaseous mixture, an explosion occurred just after the wire became visibly red. Doubtless, in the latter case, the surface over which interaction extended was sufficiently large to raise the velocity of change to the explosive rate, owing to the condensing effect exercised by the platinum; and the silver had no effect, because it is destitute of the power which platinum possesses in so high a degree of attracting gases and of acting as a catalyst.

In making this statement, I wish it to be understood that I assume that platinum *per se* would be without effect. I feel almost confident, in fact, that if they could be dealt with, even free atoms would not associate in the absence of a composite electrolyte, as it appears to me probable that at least one function of the composite electrolyte is to provide the "mechanism" by means of which the energy of chemical change is frittered away. Ostwald, in his lecture on "Catalysis" (an English translation of this is to be found in *Nature*, April 3, 1902), defines a catalyst as any substance which alters the velocity of a chemical action without appearing in the final product. I conceive, however, that the catalyst determines the interchange from its beginning. I have discussed a number of "catalytic" phenomena—including those of fermentation and of the dissolution of metals in nitric acid—in the address referred to later on.—*Note, added May 2*].

It appears to me that Brereton Baker's results lead to far-reaching consequences—that they justify, not only the conclusions I have drawn as to the conditions which determine the occurrence of chemical change, but also the conclusion already stated by me in the note previously referred to, in 1893, that *pure gases should be perfect dielectrics*; *i.e.*, that the passage of an electric discharge through a gas, like that of an explosive wave through, say,

* A Paper read before the Royal Society, May 1, 1902.

a mixture of hydrogen and oxygen gases, can only take place if an electrolyte be present, such electrolyte being, it would seem, always a composite system, and one which may be pictured as existing momentarily in a quasi-liquid state.

The argument was more fully developed in my Presidential Address to the Chemical Society, in 1895, in which I discussed very fully the nature of chemical change, and the conditions which determine it, from various points of view.

(No more striking evidence that the occurrence of a discharge in a gas is dependent on the presence of a something besides the gas—on the formation of a complex conducting system—could be given than is afforded by the beautiful experiment exhibited by Dewar at the Royal Institution, showing that the discharge at once ceases in one of Crookes's phosphorescent tubes on cooling with liquid oxygen. Such treatment cannot be supposed to cause the condensation of the residual air, but may well condition the deposition of the traces of vapour (? of conducting water) present in the gas, thereby destroying the systems within which conduction can alone occur. It may be here pointed out that this argument is perhaps also at least partially applicable in explanation of the erratic behaviour of the discharge in vacuum tubes. If the discharge occur within a complex system, it may well be that certain conditions will favour the formation of a conducting system including one, and others of a system including another, of several substances present in a tube—such an explanation, for example, would account for the fact that the mercury spectrum is only sometimes seen in tubes connected with a mercury pump. And having regard to the fact that a gas may exhibit several spectra, it may be that the spectrum of a given substance varies more or less according as it is included in one or other of several conducting systems.—*Chem. Soc. Trans.*, 1895, 1141).

No attempt has been made as yet to deal practically with the problem of electrical discharge in gases in the way in which Dixon, Brereton Baker, and Shenstone have dealt with that of chemical change. Vacuum tubes are invariably made of soft glass—which is altogether unfitted for accurate experiments, as it is always more or less readily attacked by moisture, yielding up traces of alkali; no special care is taken in cleansing them; no special precautions are used in filling them; and both oil of vitriol and commercial phosphoric anhydride are used as drying agents, although it is well known that these may be fruitful sources of contamination. And the electrodes offer special difficulties, which it may be impossible to overcome, owing to the readiness with which metals occlude gases.

If there be evidence to show that the discharge in vacuum tubes is conditioned by the presence of impurities, as I contend there is, it is open to question whether most, if not all, of the effects attributed to the so-called radiant matter—or as Sir William Crookes now expresses it, to electrons—are not in reality due to ordinary gross matter. To take an example from this author's recent communication to the Society on "Radio-activity and the Electron Theory," at the close of the paper reference is made to the discharge from a silver pole of *electrons* which cause the glass against which they strike to glow; at the same time, the silver volatilises and is deposited near the pole. "While the volatilisation of the pole is rapidly proceeding, the metal glows as if red hot. This 'red heat' is superficial only." It appears to me possible to give a more ordinary explanation of the remarkable phenomenon thus described by Sir William Crookes. A silver electrode would be more or less "polarised" with oxygen—for we know that silver has the power of absorbing oxygen when fused, and that the gas is only partially extruded as the metal cools; in any case a minute amount of oxygen would be present in the tube. When heated by the discharge *in vacuo*, the silver-oxygen "compound" would

dissociate—i.e., oxygen would be given off, but would be in part re-absorbed, so that the silver would never be entirely free from oxygen; the change, in fact, would oscillate about a point of equilibrium, and would never be total in the direction corresponding to the complete deoxidation of the silver. May not the bombardment of the glass described by Sir William Crookes have been effected by the displaced oxygen molecules, and may not the surface heating of the pole have been an outward and visible sign of the return of the truants to their silvery home?

A diamond pole, such as Sir William Crookes speaks of, might behave in a similar manner in presence of a minute amount of oxygen; in fact, the argument applies generally to the occlusion of hydrogen and other gases by electrodes.

An argument which I think will sooner or later be regarded as of weight in favour of the view that the phenomena are electrolytic in their origin, is afforded by the luminous manifestations in vacuum tubes. These can scarcely be either mere collision effects, or mere heat effects. It has long seemed to me that luminosity and line spectra are the expression—the visible signs—of the changes attending the formation of molecules from their atoms, or, speaking generally, that they are *consequences of chemical changes*, a chemical change being one which involves an alteration of molecular composition, or it may be of molecular configuration, as it is conceivable that even changes involving but the formation of isodynamic (tautomeric) molecules—changes in molecular structure unattended with change in molecular size—may give rise to such manifestations. Dealing with the question of the luminosity of hydrocarbon flames, I expressed this view in 1895 in the terms given below.

("Interest should be revived in the subject by the recent observations of V. B. Lewes (*Roy. Soc. Proc.*, 1895, vol. lvii., p. 450) on the decomposition of acetylene at high temperatures, which have led him to suggest that this compound plays the chief part in promoting luminosity in hydrocarbon flames, and that the heat liberated during its decomposition endows the carbon particles produced from it with an incandescence far higher than corresponds to the temperature of the flame. It appears to me that while accepting this as a partial explanation, it is unnecessary to suppose that luminosity is consequent on the production of presumably solid carbon particles; the conversion of acetylene, or other hydrocarbons, at high temperatures into hydrogen and carbon, although a decomposition in the ordinary sense of the term, is doubtless a change involving the interaction of several molecules, and the consequent formation of carbon molecules of a high order of complexity together with hydrogen molecules; and it is exothermic because the energy liberated in the combination of the carbon atoms among themselves, and also of the hydrogen atoms, is far in excess of that absorbed in the decomposition of the hydrocarbon molecules. The initial luminance may therefore well be that of the molecules at the moment of formation prior to condensation, although the continued incandescence of the carbon molecules after their reduction to the solid state probably contributes largely to maintain luminosity, giving to hydrocarbon flames their special value, perhaps. But this is to explain the phenomena in terms of Frankland's theory, as I understand it, and as appears to be necessary in order to explain the luminous appearance of a hydrogen-oxygen flame burning under pressure, and other cases in which the products of combustion are gaseous."—*Chem. Soc. Trans.*, 1895, p. 1147).

In the discussion on Mr. Campbell Swinton's paper on the luminosity of the rare earths when heated *in vacuo* by means of cathode rays, read in April, 1899 (*Roy. Soc. Proc.*, vol. lxx., p. 115), I applied this view in explanation of the brilliant luminosity of certain rare earths, and also of the electric arc, suggesting in the latter case that the carbon molecules were dissociated by the passage of the

current, and that the re-association of the atoms into molecules gave rise to the intensely luminous effect which is characteristic of the arc.

Bunte has argued (*Deut. Chem. Ges. Ber.*, 1898, p. 5), in the case of the Auer von Welsbach gas mantle, that the high luminosity is not so much due to a specific superior radiating power of the earth used as to the fact that, in virtue of the power which a substance such as ceria possesses of forming a peroxide, combustion takes place to a greater extent at a surface on which it is present than on one consisting of a neutral oxide; consequently, the temperature is higher at such a surface. This undoubtedly must be the case; but I would go further, and regard the chemical changes occurring at the surface as the direct seat, or origin as it were, of the luminosity. Probably, a higher oxide is alternately decomposed and reformed—in other words, the process is one of oscillatory or re-current oxidation. Owing to the influence which the oxide exercises as a catalyst combustion doubtless takes place at its surface more completely than it would at a corresponding neutral surface, and in consequence the temperature developed at the oxide surface is above that of the flame generally.

[It is noteworthy that besides ceria, which is by far the most efficient, only one or two other oxides are effective excitants; and that cerium dioxide is remarkably stable at high temperatures.—*Note, added May 2*].

A similar explanation may be applied to the incandescence of oxides generally, such as is witnessed, for example, in the lime and zirconia lights. The Nernst lamp probably owes its efficiency to a like cause. It may well be that in the case of the incandescent mantle the maximum effect is produced when only a relatively small proportion of active oxide is present, because at the particular state of dilution the oxide is present in solid solution in a form in which it is most prone to suffer change—that besides being placed under the necessary conditions of freedom, it attains to the most suitable degree of molecular complexity, and therefore to its greatest activity in dilute solid solution, just as many substances do in dilute liquid solutions.

Mr. Campbell Swinton's observations appear to me to be in harmony with these conclusions. An intensity of cathode rays that gave a brilliant light with "pure" thoria and with a mixture of 99 per cent thoria with 1 per cent ceria was found by him to give practically no light with "pure" ceria and with a mixture of equal parts of thoria and ceria. It is improbable that Mr. Swinton dealt with pure thoria, as the methods of purification practised at that time did not suffice to give a pure product. That thoria alone gave more light under the influence of cathode rays than in the Bunsen flame may have been due to the fact that it was more intensely heated in the former case, the effect produced by minute proportions of the exciting oxide being much dependent on temperature, and greater the higher the temperature.

The need of an explanation such as is here given of the luminosity of oxides at high temperatures has, I know occurred to others. My colleague, Professor Ayrton, has long held such a view, and he informs me that, in the course of conversation with him in 1897, Professor Elihu Thomson gave it as his opinion that the brilliant incandescence of lime in the oxy-hydrogen flame was not a mere high temperature effect (compare *Journal of the Society of Arts*, February 10, 1899, p. 256; E. Pringsheim, *International Physical Congress at Paris*, "Report 2").

The phenomena of phosphorescence under the influence of the electric discharge exhibited by the oxides and basic sulphates of the rare earths, with which Sir William Crookes's classical researches have made us familiar, may be included in the same category with those above discussed; if not due to recurrent oxidation, they may be cases of recurrent polymerisation. Apparently the same oxides act as excitants whether a flame or cathode rays be used. Sir William Crookes, it is well known, holds the view that yttria, lanthana, &c., are characterised by

definite phosphorescent spectra; on the other hand, Lecoq de Boisbaudran has contended that the yttria and gadolinite earths are not self-luminous. This latter view has recently been confirmed by Baur and Marc (*Deut. Chem. Ges. Ber.*, 1901, p. 2460). According to these observers, whilst the colourless oxides and salts of yttrium, gadolinium, and lanthanum are not specifically luminescent, if mixed with minute proportions of the earths which have coloured salts, viz., erbium, neo- or praseodymium, they afford spectra such as have hitherto been regarded as characteristic of themselves; and such spectra may be equally well developed by using lime or calcium sulphate as diluents; yttria itself, however, fails to give a spectrum when mixed in small proportion with lime.

[If it should eventually be established that the emission spectra are conditioned solely by "earths" which afford coloured salts, as the emission spectra appear to be closely related to the absorption spectra, dark lines in the one taking the place of bright lines in the other, it will be possible to correlate the production of visible colour with that of a luminous spectrum, and to regard both as originating in the same intramolecular mechanism.—*Note, added May 2*].

The argument may be carried a stage further and applied to phosphorescent phenomena generally. It appears possible to regard all these as the outcome of oscillatory changes in molecular structure—and the slow decay of the effect which is observed in many cases may be compared with the slow discharge of a condenser—the charging of which be it noted may be regarded as but a process of molecular deformation of the dielectric.

(To be continued).

HISTORY OF THE SYNTHESIS OF INDIGO.*

By AD. BAEYER.

HAVING been asked to give a history of the synthesis of indigo, I would first remark that I have already published, twenty years ago, an account of my work on indigo; at that time I wrote as follows (*Berichte*, vol. xiii., p. 2254):—"The discovery of an easily performed synthesis of indigo blue (starting with chlorised isatin) having closed an important chapter in the history of this colouring material, I take the opportunity of glancing over the course of my research which has led to this result. This research is described in a large number of isolated notes not having any apparent connection, and I think I can be of service to my colleagues by showing, on the one hand, that the discovery of artificial indigo has been the fruit of a long series of experimental researches, systematically and intimately connected together, and by particularising, on the other hand, the line of work I am adopting at the present time based on the facts discovered by myself and my pupils."

Indol, extracted for the first time from indigo, acquired great importance in physiological chemistry from the fact of its formation in the animal organism.

Isatin, discovered simultaneously by Erdmann and Laurent, furnished aniline to Hofmann by fusion with potash, and enabled him to prepare the mono- and dichlorised, and mono- and dibromised anilines. It was, further, the starting-point of my work on indigo. In the paper just quoted the following words are to be found:—"The first problem I set myself was to eliminate the oxygen from isatin, and we know how it was solved in 1865 and 1866 by the transformation of isatin into dioxindol, oxindol, and indol. The enormous expense of time and work entailed by the discovery of the method of reduction by zinc powder, a method necessary to realise

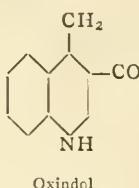
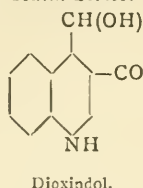
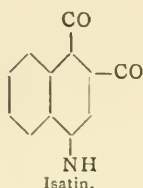
* Abridged from the Report of the Conference held on the occasion of the Inauguration of the Hofmann Institute at the German Chemical Society.

the desired end, was further recompensed by the discovery in 1868 of *artificial alizarin* in my own laboratory by my assistant Graebe, and M. Liebermann."

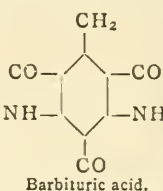
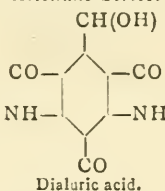
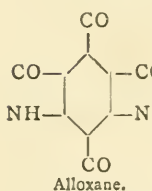
While studying one day the properties of isatin, I was struck by the great analogy which existed between it and alloxane. The reduction of isatin, made by Laurent and Erdmann in 1840, did not go beyond the first phase, isathyde, as the other derivatives discovered by these chemists, indene, hydrindene, &c., were only complex products of condensation.

But there was a hope that the chain of thought which had led to malonyl urea would also be of service in the case of isatin. This hope was realised when, in 1865, I took up the research on isatin with my pupil C. A. Knop. By successively treating isatin with sodium amalgam and tin and hydrochloric acid, we obtained dioxindol corresponding to dialuric acid, and, finally, the ultimate term of the series corresponding to barbituric acid, viz., oxindol.

Isatin Series.



Alloxane Series.



The above formulæ for alloxane were adopted from my work on uric acid, and still hold good.

But an idea occurred to me during the research which prevented me from recognising that the derivatives of isatin were constituted in a very analogous manner. The phenolic properties of oxindol led me to consider it as the phenol of a hypothetical compound, to which I assigned the formula—



and to which I gave the name of *indol*. I immediately attempted the preparation of the hypothetical indol. I started with oxindol which only contained one atom too much oxygen, and which behaved like phenol. After six months of unsuccess I confided my trouble to my colleague Stahlschmidt, and from him learned that zinc powder had been for some time used as a reducing agent. I at once made the experiment, but the oxindol resisted all my efforts, until in despair I heated some almost to redness with zinc powder in a combustion tube. At last I had in my hands the substance from which indigo is made.

In my paper in 1880 I wrote:—"Henceforth all my efforts were turned to the discovery of a simple method for the preparation of indol, as I considered it as the true source of the indigotic group. In 1868 a direct method was found for obtaining indol by the action of zinc powder on indigo blue, and in 1869 a synthetical method starting from nitrocinnamic acid and its derivatives (*Berichte*, vol. ii., p. 679). This latter paper contains a passage which I quote in full as it contains the complete programme of my work on indigo up to the present time: 'If we wish to prepare indol synthetically it is necessary, according to the above formulæ, to introduce a lateral chain into the benzenic radical, formed of two carbon links, and one atom of nitrogen, and to join them together. The conditions

necessary for effecting this operation are found in nitrocinnamic acid, if we abstract the carbonic acid and the oxygen from the nitrated group. And, in fact, we have found that when fused with potash, nitrocinnamic acid gives indol.'"

For convenience of handling, I have now arranged my materials, not in chronological order, but in order of importance, viz., indol, isatin, indigo. The study of indol helped to found the theory of the closure of chains, that of isatin to establish desmotropic isomerism, and the work on indigo led to a whole series of new methods which were utilised later on.

The History of Indol.

Before this substance was discovered I gave it the following formula:—



When I had obtained it, I noticed a great analogy between indol and pyrrol, and endeavoured to determine the constitution of this latter body (*Berichte*, vol. ii., p. 99). We discovered pyrrolate of potassium, and from it deduced the formulæ of pyrrol, indol, and furfuran. My synthesis of indol was, however, interpreted in a different manner by other chemists. Up to 1879, indol had only been prepared by using high temperatures, but during this year I found a method which enabled me to obtain indol by the wet way. After the transformation of isatin, by the action of pentachloride of phosphorus, into chlorised isatin, and the conversion of this latter, by reduction, into indigo, I submitted oxindol to the same treatment. The first reaction was easily obtained, but dichlorised indol was formed instead of the monochlorised product.

The substitution of hydrogen for the chlorine offered the greatest difficulties, and could not be effected by zinc powder, or hydriodic acid, on account of resinification, while sodium amalgam or sodium in etheral or alcoholic solution would not attack the chlorine. But by heating the dichlorised product to boiling in alcoholic or, better still, amyl solution, and introducing small pieces of sodium, I succeeded in attaining my end. This led to the synthesis of quinolein from cinnamic acid, and thus revealed the relation between indol and quinolein. About the same time the law governing the closure of chains was recognised which is at the basis of this synthesis.

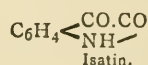
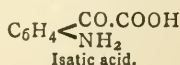
The researches on oxindol, containing two atoms of oxygen in the lateral chain, led me to submit to the same treatment bodies of the same nature, but containing three atoms of carbon, carbostyryle and hydrocarbostyryle. The latter easily gave a dichlorised quinolein corresponding to the twice chlorised indol; but with a greater number of carbon atoms in the lateral chain the cyclic closing could not be obtained.

My attempts to prepare orthonitrophenylacetic aldehyde by the method indicated in a note published in 1880 were unsuccessful, but, on the other hand, they led to the discovery of the synthesis of indigo, starting from ortho-nitrocinnamic acid.

Contribution to the History of Isatin.

By the reduction of isatin to indol, I gained the certain knowledge that this class of body was formed by the products of the oxidation of indol. I considered isatin to be an orthoquinone, although at that time no compound of this class was known, and at the same time I gave the formulæ of a pyrocatechin, and a phenol derivative, to dioxindol and oxindol; this turned out to be quite correct.

Soon afterwards Kékulé criticised my theories, and submitted the hypothesis that indol was an orthoamino-phenylacetylene, dioxindol an aldehyde, isatinic acid an aminised derivative of benzoylformic acid, and isatin an anhydride of this acid. He gave the following formulæ to isatinic acid and isatin:—



His conception of isatic acid and the relations between it and isatin were quite new. It showed a way for the synthesis of isatin, on which he expressed himself as follows:—

"I am engaged in transforming phenylacetic acid, first into bromophenylacetic acid, and then into nitrobromophenylacetic acid. By the reduction of this latter there will be formed probably orthoamidophenylacetic acid, and at the same time a body corresponding to carbostyryl. If we succeed in oxidising this acid in such a manner that the hydrogen of the lateral chain is replaced by oxygen, we shall obtain isatic acid and isatin."

Kékulé wished, by the introduction of bromine, to put the nitro group into the ortho-position, but his pupil was not able to effect this.

Eight years elapsed after Kékulé's first publication without any appreciable results being obtained, when I undertook to test the truth of his ideas. I said to myself that if isatin was really the anhydride of isatic acid, the products of the reduction of the latter would be to the products of the reduction of isatin as the acid itself is to its anhydride.

As isatic acid is only stable in alkaline solution and cannot be reduced under these conditions, we first acetylated it, and then reduced the stable acetylated derivative in acid solution by means of sodium amalgam in acetic solution. In this manner acetylhydric acid was obtained, and by the further reduction of this *oxindol*. The slightly enlarged conception of Kékulé having been thus confirmed, we were able to proceed to the realisation of his programme for the synthesis of isatin.

Profiting by a remark of Radziszewski, that the ortho-nitrated acid forms in large quantities at high temperatures, I conducted the nitration on the boiling water-bath, and obtained a good return of the substance so long sought for in vain. As could be foreseen, the reduction of this acid gave synthetic oxindol, and the amido-oxindol prepared from this latter was easily transformed by oxidation into isatin. Thus, on June 6, 1878, I realised, for the first time, the synthesis of isatin. The transformation, discovered in 1870, of isatin into indigo was thus completed, and finished the entire synthesis of the colouring material.

During the next year, my work produced a new product of the reduction of isatin, viz., hydroisatin. The solution of isatin and of its acetylated derivative in glacial acetic acid is decolourised by zinc powder; water precipitates a white substance, which, when exposed to the air, is again transformed into isatin. But if we boil an aqueous solution of isatin, treated with a little hydrochloric acid, with zinc powder, after a short while there is a persistent decoloration, with the formation of oxindol. Hydroisatin should therefore be considered the first product of the reduction of isatin.

The transformation of Kékulé's isatin into my hydroisatin corresponded to the reduction of phenanthrene quinone into dioxphenanthrene. With the di-ketonic formula it was difficult to conceive that the two atoms of oxygen could be reduced simultaneously with the formation of a double bond which had not previously existed. A special hypothesis was necessary according to which the two ketonic oxygens in the ortho- and para-positions should influence each other mutually. The merit of having raised this hypothesis to the position of a general law is due to J. Thiele.

I had observed, with Rupe, that in the reduction of muconic acid, the two atoms of hydrogen were fixed to the ends of the hydrocarbonised chain contained in this acid, and, at the same time, a new double bond was formed in the centre of the chain.

I explained this particular phenomenon by the attraction the carboxylised groups had for the atoms of hydrogen. Thiele put forward the hypothesis that two double bonds, close to each other, were possessed of a particular structure which required a new symbol to express it. A pair of double bonds could be compared to a magnet which is

only active at its extremities; when cut in half it forms two magnets, and when made into a ring it loses its external power of acting. By admitting this as true, hydroisatin should be looked upon as an isomer of dioxindol; that is to say, as the true dioxindol corresponding to pyrocatechin. The substance which had before received the name of dioxindol results from the transposition of hydroisatin, according to Erlenmeyer's rule, and it is to this transposition, which it was impossible to foresee, that we must attribute the fact that the nature of this class of compounds remained obscure for so long.

Researches carried on with Oekonomides in 1882 showed that in the ethers of isatin, prepared by means of the silver salt, the alcoholic radicals were fixed to the oxygen, while acetyl-isatin could only contain the acid radical joined to the nitrogen. Consequently, isatin reacts in two different manners, a phenomenon called tautomerism by Laar later on; these two forms I called *lactame* and *lactime*, and I consider that it is most probable that in the solid state isatin is a lactame, while it does not appear to me to be impossible that the solution may also contain a lactime modification.

In 1883 I published this theory with regard to indoxyl, and expressed myself as follows:—"Isomers are only known in the combined state; in the free state they return spontaneously to their initial form. Their instability should be attributed to the mobility of the hydrogen atoms, assuming that the substitution of other groups for the hydrogen renders the compounds stable."

Contribution to the History of the Artificial Preparation of Indigo.

Artificial indigo first saw light in the year 1870, when, in collaboration with Emmerling, I succeeded in transforming isatin into indigo blue by the action of trichloride of phosphorus containing free phosphorus. As, at this time, isatin could only be prepared from indigo itself, this synthesis did not become complete until I succeeded on June 6, 1878, in preparing isatin artificially from phenylacetic acid. Shortly after my first publication Emmerling and Engler observed traces of indigo formed from materials not originally made from the colouring matter, by heating the syrupy mass obtained as a by-product in the nitration of acetophenone, with zinc powder and soda lime, by the method I used for the transformation of nitrocinnamic acid into indol. They were of the opinion that indigo was an azoic colouring matter, and that seemed experimentally correct, but I looked upon indigo as an oxygenated derivative of indol. As they obtained a trace of indigo, although with very great difficulty, the way seemed open for its synthesis from acetophenone.

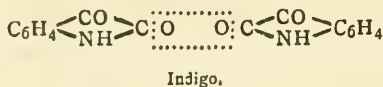
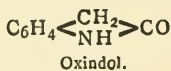
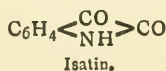
Later on, however, they were unable to repeat their experiment, and six years later they wrote:—"We frankly state that one of us has not succeeded—after repeating the nitration experiment innumerable times with the most diverse kinds of fuming nitric acid, and under the most varied conditions—in obtaining a syrupy nitrated product, which, like that previously prepared, would remain syrupy for several weeks; and it is exactly this syrupy product that we require as a starting point. . . . In face of the refutation of our synthesis of indigo blue by Wichelhaus we are powerless, inasmuch as, in spite of reiterated experiments, we have not been able to succeed in reproducing the conditions under which we obtained the indigo, and that the method in question did not enable us to produce the indisputable proof of our synthesis; that is to say, to prepare a quantity of the substance for analysis."

The merit of having discovered a synthesis of indigo is due, I think, to Nencki, who, in 1875, observed that indol, suspended in water, gave traces of indigo when treated with ozone.

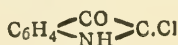
The considerations which led me, thirty years ago, to the preparation of artificial indigo from isatin were the following:—"One of the most important problems of the chemistry of indigo is the preparation of this colouring matter from isatin. Although isatin could only be reduced

to the state of isathyd, there were hopes that the problem might be solved by the further reduction of isatin. But the work done in collaboration with Knop made known a whole series of products of reduction of isatin, and we even succeeded in removing the whole of the oxygen from isatin without obtaining a single reaction leading to indigo blue. The hope of effecting the synthesis of indigo seemed therefore to become less and less. If we consider the nature of the reagents employed up to the present for the reduction of isatin, we see that they are all *hydrogenating* agents, and that there has not been a body used capable of removing the oxygen from the isatin without hydrogenating this latter. This method alone offered some chance of success, and, in fact, experiment showed that for the reduction of isatin into indigo blue it was necessary to totally exclude hydrogen, as the action of this element led to a series of entirely different compounds which could not be transformed into indigo. A reagent which realises these conditions is trichloride of phosphorus containing free phosphorus."

These considerations were fully confirmed by experiments made later on. In the reduction of isatin to oxindol, it is precisely the atom of oxygen necessary for the formation of indigo that is replaced by the hydrogen. On the other hand, the phosphorus leaves this atom of oxygen intact, and, by eliminating the other atom of oxygen from the isatin, leads directly to the formation of indigo, as the following formulæ show:—



In the years 1878-1879 I found that the synthesis of indigo could be improved by starting with chloride of isatin; the reduction of this body probably depends on the addition of two atoms of hydrogen with the formation of chlorised indoxyl, which is transformed directly into indigo by the loss of hydrochloric acid:—



This indoxyl was discovered simultaneously by Baumann and Tiemann in 1879, and oxindol should be considered even more as the true mother-substance of indigo, as its formation always preceded that of indigo in nearly every synthesis.

Baumann first called attention to the fact that indicone from urine was different to the vegetable indicone obtained by Schunck. Later on, in collaboration with Brieger, he showed that indicone contained a substance named indoxylsulphuric acid, in the examination of which he was associated with Tiemann.

These two chemists then found that, as with phenol-sulphate of potash, indolsulphate of potash was split up by acids into sulphuric acid and a body of a phenolic nature, indoxyl. Treated with an oxidising agent, indoxyl was transformed almost quantitatively into indigo. I found the same properties for indoxyl prepared later on synthetically. The formula they assigned to indoxyl is still used; they rightly compared the transformation of indoxyl into indigo with the transformation of dimethyl-pyrogallol ether into cerdriret, but they placed the double bond produced by the formation of the colouring material in the benzenic instead of the pyrolic radical, and thus arrived at a formula for indigo which does not agree with the properties of this body.

To them, however, is due the merit of having discovered indoxyl and showing its easy transformation into indol. I, on the other hand, did not agree with them at first, and

only recognised the truth of their observations two years later, after having prepared indoxyl synthetically, and established its identity with that obtained from urine.

The idea of using the synthesis of indigo commercially did not arise till 1880, when I commenced using cinnamic acid instead of phenylacetic acid.

In the course of an experiment instituted with a view to prepare orthonitrophenylacetic aldehyde, I boiled the bromide of orthonitrocinnamic acid with alkalis, and found that a small quantity of indigo was formed. The study of this reaction led me to the discovery of orthonitrophenylpropionic acid and to the transformation of that body into indigo. This invention was patented on March 19, 1880, and was published for the first time in December of the same year.

My researches were considerably helped by the numerous works on cinnamic acid published during the period between 1860 and 1880. The extensive researches of Glaser, Beilstein, and Kuhlberg on orthonitrocinnamic acid were particularly useful to me.—*Moniteur Scientifique*, Series 4, vol. xv. p. 145.

CHEMICAL SOCIETIES OF THE NINETEENTH CENTURY.*

By HENRY CARRINGTON BOLTON, Ph.D.

(Concluded from p. 232).

GREAT BRITAIN.

SOCIETY FOR PHILOSOPHICAL EXPERIMENTS.

FOUNDED in 1794 at London.

Publication.—Minutes of the Society for Philosophical Experiments, 1794.

NOTE.—A German translation of the *Minutes* was edited by Alex. Nic. Scherer and published at Halle in 1803.

CHEMICAL SECTION OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Founded in 1831. This is, however, a corporate part of the British Association, and the papers read to the Section are published in the annual Reports of the British Association, 1831-1900. In 1900: President, W. H. Perkin, jun.; number of members not given.

CHEMICAL SOCIETY OF LONDON.

Founded in 1841 at London. In 1900: President, T. E. Thorpe; honorary and foreign members, 33; members, 2300.

Publications.—Memoirs and Proceedings of the Chemical Society of London (1841-48); Quarterly Journal, 1849-62; Journal of the Chemical Society, 1863-1900.

SOCIETY OF PUBLIC ANALYSTS.

Founded in 1874 at London. In 1900: President, Walter W. Fisher; honorary members, 9; members, 260.

Publication.—Proceedings of the Society of Public Analysts, 1876; The Analyst, 1877-1900.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Founded in October, 1877, in London; incorporated, 1885. In 1900: President, John Millar Thomson; members, fellows, and associates, 1008 (resident members, 904); students, 118. Total, 1126.

Publications.—Proceedings, half-yearly, 1878-1900; Register, yearly, 1878-1900; Regulations, yearly, 1878-1900.

* Read at the Twenty-fifth Anniversary of the American Chemical Society, held in New York City, April 12-13, 1901. From advance proofs of the *Smithsonian Miscellaneous Collections*, 1901.

SOCIETY OF CHEMICAL INDUSTRY.

Founded in 1881 at London. In 1900: President, Charles F. Chandler; honorary member, 1 (John Glover); members, 3459.

Publication.—Journal of the Society of Chemical Industry, 1882-1900.

NOTE.—The Society has eight Sections—London, Liverpool, Manchester, Newcastle, New York, Nottingham, Scotland, and Yorkshire.

SOCIETY OF DYERS AND COLOURISTS.

Founded in 1884 at Bradford. In 1900: President, H. Grandage; honorary members, 3; members, 553.

Publication.—Journal of the Society of Dyers and Colourists, 1884-1900.

ALEMIC CLUB.

Founded in 1889 at Edinburgh. This is a private club of only six members and has no president; the Secretary is Leonard Dobbin.

Publishes no journal, but has issued 15 Reprints of Chemical Monographs, &c., 1893-1900, and other works.

INTERNATIONAL ASSOCIATION OF LEATHER-TRADES CHEMISTS.

Founded September, 1897, at London. In 1900: President, H. R. Procter; number of members, —.

Publication.—Report of the Proceedings of the Conference of Leather-Trades Chemists, 1897.

ITALY.

ASSOCIAZIONE CHIMICO-FARMACEUTICA FIORENTINA.

Founded in 1877 at Florence. In 1900: honorary members, 20; resident members, 100.

Publication.—L'Orosi, Bollettino di chimica, farmacia e scienze affini. Firenze, 1878-1900.

SOCIETÀ CHIMICA DI MILANO.

Founded in February, 1895, at Milan. In 1900: President, Angelo Menozzi; resident members, 152; correspondents, 133.

Publication.—Annuario della Società chimica di Milano, 1896-1900.

ASSOCIAZIONE CHIMICO-INDUSTRIALE DI TORINO.

Founded June 25, 1899, at Turin. In 1900: President, Vittorio Sclopis; honorary members, 4; resident members, 103; correspondents, 87.

Publication.—La Chimica industriale, 1899-1900.

SOCIETÀ ITALIANA DEI CHIMICI ANALISTI.

Founded in 1893 at Pavia.

Publication.—Atti ufficiale delle Società italiana dei chimici analisti, 1893. This forms a pamphlet of 18 pp. only, and is perhaps a mere prospectus, as the Society ceased to exist before 1900.

JAPAN.

CHEMICAL SOCIETY OF TOKYO.

Founded April, 1878, at Tokyo. In 1900: President, Naokichi Matsui; number of members, 156; associates, 197.

Publication.—Tokyo Kagakkai Kaishi, 1880-1900.

SOCIETY OF CHEMICAL INDUSTRY OF JAPAN.

Founded February, 1898, at Tokyo. In 1900: President, Takeaki Enomoto; honorary members, 7; members, 223; associates, 429.

Publication.—Kōgyō Kagaku Zasshi, 1898-1900.

RUSSIA.

RUSSKAGO KHMICHESKAGO OBSHCHESTVA
(Russian Chemical Society).

Founded October 26, 1868. The Chairman of the first meeting was D. Mendelëff. In 1900: President, F. F. Petrushevsky; members, 327.

Publications.—Zhurnal Russkago Khimicheskago Obshtchestva. St. Petersburg, 1869-72, 4 vols.

Continued as—

Zhurnal Russkago Khimicheskago Obshtchestva i Fisicheskago Obshtchestva, 1873-78. 6 vols.

Continued as—

Zhurnal Russkago Fisiko-Khimicheskago Obshtchestva, 1879-1900.

SOUTH AFRICA.

CHEMICAL AND METALLURGICAL SOCIETY OF
SOUTH AFRICA.

Founded May, 1894, at Johannesburg.

Publication.—Proceedings of the Chemical and Metallurgical Society of South Africa, 1894-1897

SWITZERLAND.

SOCIÉTÉ CHIMIQUE DE GENÈVE.

Founded February 10, 1878, at Geneva. In 1900: President, F. Kehrmann.

Publication.—The Minutes of the monthly meetings are published in Archives des sciences physiques et naturelles de Genève, and in the Chemiker Zeitung.

VEREIN SCHWEIZERISCHER ANALYTISCHER CHEMIKER.

Founded March 12, 1887, at Zürich. In 1900: President, A. Bertschinger; number of members, 94.

Publication.—The organ of the Society is Schweizerische Wochenschrift für Chemie und Pharmacie, which was established under the title Schweizerische Zeitschrift für Pharmacie, 1856-62.

UNITED STATES OF AMERICA.

CHEMICAL SOCIETY OF PHILADELPHIA.

Founded in 1792 at Philadelphia, under the presidency of James Woodhouse. Number of members unknown. The Society was in existence for more than ten years.

Publication.—Memoir on the Supply and Application of the Blowpipe (&c.), by Robert Hare, 1802.

COLUMBIAN CHEMICAL SOCIETY OF PHILADELPHIA.

Founded August, 1811, at Philadelphia, under the presidency of James Cutbush; honorary members, 69; junior members, 13.

Publication.—Memoirs of the Columbian Chemical Society of Philadelphia. Vol. I., 1813.

CHEMICAL SECTION OF THE AMERICAN ASSOCIATION FOR
THE ADVANCEMENT OF SCIENCE.

A migratory organisation, founded in 1875 as a Sub-Section; it became Section C of the A. A. A. S. in 1882 at the second meeting in Montreal. In 1900: Chairman of the Section, Jas. Lewis Howe; members, 89; fellows, 181.

Publications.—The Proceedings of the A. A. A. S. has a division containing papers read before the Section of Chemistry.

AMERICAN CHEMICAL SOCIETY,

Founded April 20, 1876, in New York City. In 1900: President, William McMurtre; honorary members, 10; members, 1546; associates, 123.

Publications.—Proceedings of the American Chemical Society, 1877-78; Journal of the American Chemical Society, 1879-1900.

NOTE.—In 1900 the Society had twelve Sections:—Rhode Island, Cincinnati, New York, Washington, Lehigh Valley, Chicago, Nebraska, North Carolina, Columbus, North Eastern, Philadelphia, and Michigan.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

Founded September 8, 1884, at Philadelphia. In 1900: President, B. W. Kilgore; members, 350.

Publications.—Methods of Analyses, 1884-88; Proceedings, 1889-1900.

NOTE.—Conventions of the Official Agricultural Chemists had been held prior to 1884: in 1880, at Washington and Boston; in 1881, at Cincinnati; and in May, 1884, at Atlanta.

CHEMICAL SOCIETY OF WASHINGTON.

Founded at Washington in 1884. In 1893 became the Washington Section of the American Chemical Society, retaining also its name as above. In 1900: President, H. Carrington Bolton; members, 114.

Publication.—Bulletin of the Chemical Society of Washington, 1884-1892.

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS.

Founded February 19, 1898. Meetings are held in New England. In 1900: President, Rufus P. Williams; honorary members, 8; active members, 50; associates, 22.

Publications.—Circulars of Information and Reports, 1898-1900. Also Registers.

VICTORIA.

SOCIETY OF CHEMICAL INDUSTRY OF VICTORIA.

Founded in 1900 under the Presidency of Orme Masson; membership, about 100.

ADDENDUM.

SOCIÉTÉ D'ARCEUIL.

Founded in 1807 at Arcueil. Dissolved in 1822. Members (at any one time), 12.

Publication.—Mémoires de physique et de chimie. Paris, 3 vols., 8vo. 1807-17.

NOTE.—This private organisation was founded by C. L. Berthollet; the meetings were held at his country house in Arcueil, near Paris. The membership included La Place, C. L. Berthollet and his son A. B. Berthollet, Biot, Gay Lussac, Humboldt, Thénard, Decandolle, Collet-Descotils, Berard, Chaptal, Dulong, Poisson, Malus.

The foregoing list does not include Academies of science nor Associations of general science (with a few exceptions); it does not embrace societies having for their object industries involving chemical processes in part, except the refining of sugar; nor does it include the numerous societies of brewers and of beer-making, among which may be named the following:—

BRÄU-INDUSTRIE VEREIN IM KÖNIGREICH BÖHMEN, founded at Prague in 1874, and publishing the Böhmisches Bierbrauer.

DEUTSCHE BRAUERBUND, founded at Nürnberg in 1861, and publishing the Allgemeine Hopfen-Zeitung.

WÜRTTEMBERGISCHE BRAUERBUND, founded at Waldsee in 1872, and publishing the Schwäbische Bierbrauer.

BADISCHE BRAUERBUND, founded at Nürnberg in 1876, and publishing the Hopfenlaube.

DEUTSCHE BRAUMEISTER VEREIN, founded at Berlin, 1887, and publishing the Deutsche Brau-Industrie.

ASSOCIATION GÉNÉRALE DES BRASSEURS BELGES, founded at Brussels in 1874, and publishing Revue des Bieres.

COUNTY BREWERS' SOCIETY, England, publishing since 1871 the Brewers' Guardian.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1902.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, May 9th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us chemically during the month, all were found to be clear, bright, and well filtered.

The abnormal drought still continues; the amount of rain that has fallen at Oxford during the month is 1.21 inches, the averagefall is 1.61 inches; this leaves a deficit of 0.40 inch, which, if added to the previous deficit for the year, brings it to 2.94 inches, or 42.2 per cent on the thirty-five years' average.

Our bacteriological examinations of 532 samples have given the results recorded in the following table; we have also examined 62 other samples, from special standpipes, wells, &c., making a total of 594 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	282
New River, filtered (mean of 132 samples) ..	9
Thames, unfiltered (mean of 26 samples) ..	10652
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 289 samples) ..	31
Ditto ditto	496
Ditto ditto	0
River Lea, unfiltered (mean of 26 samples) ..	545
River Lea, from the East London Company's clear-water wells (mean of 33 samples) ..	26

Of the 454 samples of impounded and filtered water supplied to London and examined bacteriologically during the month, 27 samples, or 5.9 per cent, were sterile. Thirteen samples contained more than 150 microbes, while thirty-one samples, or 7.0 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the thirty-one excess samples was 181, against a corresponding mean of 166 in seventeen excess samples during March. These excess samples were by no means equally distributed among the various companies.

Taken as a whole, the Metropolitan water supply more than maintains the high standard of purity which has characterised it during the previous months of this year.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

JAMES DEWAR.

A NEW INVESTIGATION CONCERNING THE ATOMIC WEIGHT OF URANIUM.*

By THEODORE WILLIAM RICHARDS
and
BENJAMIN SHORES MERIGOLD.

(Concluded from p. 239).

It is worth while to enquire whether or not the method may conceal some source of constant error beyond the reach of the experimental precautions detailed above. Such an error could hardly have occurred during the analysis; for every step of this procedure was verified by confirmatory evidence. If a flaw existed, it must have been in the purity of the original substance. Since the observed atomic weight is lower than the former results, it is important to examine into only those possible irregularities which could have had the effect of lowering the apparent value.

The probable impurities tending to lower the atomic weight are, first, sodic bromide; second, hydrobromic acid; third, free bromine; fourth, uranic pentabromide; and fifth, an unknown metal with a lesser equivalent. The first impurity was found to be present, its amount was determined, and a suitable correction was applied. The second could not have been formed during the sublimation of the uranous bromide, because compounds of hydrogen were scrupulously excluded. If formed by the action of water after the sublimation, the atomic weight would have appeared too high—for moist uranous bromide emits hydrobromic acid instead of absorbing it. The third impurity, free bromine, could hardly have been imprisoned or absorbed by the sharply crystalline salt to any appreciable extent, since the concentration of the bromine vapour in the issuing gases was but small.

The evidence in regard to the absence of pentabromide is fairly conclusive, although somewhat indirect. All attempts by many investigators to form this compound have failed, in spite of the recognised existence of the corresponding chlorine compound. It seemed possible, however, that while this compound is not formed at high temperatures, lower temperatures might permit the addition of the extra bromine. Accordingly the preparations used in Analyses 7, 8, 10, and 11, were cooled in a current of dilute bromine vapour, instead of in pure nitrogen. The presence of a comparatively small amount of pentabromide would make a very decided difference in the quantity of bromine found. Hence the essential agreement of the average result of these analyses, 238.50, with the average result of all the others, 238.52, is good evidence of the absence of uranum pentabromide.

With regard to the fifth possible impurity nothing can be said except to point out the many operations involved in the purifications. These seem to point toward probable purity; but it is nevertheless to be regretted that lack of time prevented the analysis of many different fractions of material, prepared in varying ways.

The presence of oxybromide would, of course, cause low bromine analyses, and too high an apparent atomic weight. Therefore this possible cause of error need not be considered, even if the oxybromide had ever been made in the absence of water. In the light of all these considerations, there would seem to be no good reason to question the purity of our bromide.

On comparing the result of this investigation, 238.53, with that of Zimmermann's, 239.59 (the only previous work worthy of serious consideration), the difference of over a unit seems at first to be one of great magnitude. The percentage difference (0.45 per cent) is, however, smaller than many a difference which often has been passed by unheeded in small atomic weights, such as those of magnesium or aluminum. This point illustrates the difficulty

of obtaining results with high atomic weights which can satisfy the cursory reader.

Nevertheless, such a difference is far too great to pass unchallenged. It seems highly probable that the greater part of it is due to the previously discussed sources of inaccuracy in Zimmermann's method—especially to the difficulty of wholly re-oxidising the lower oxide. The failure to oxidise half a per cent of the uranous oxide, involving an error in the weight of only 0.017 per cent of the total weight of the substance, would account for the discrepancy.

Hence it seems not unlikely that the atomic weight of uranium is really as low as 238.53. Nevertheless, the question cannot be looked upon as conclusively settled. Certainty can be obtained only by the application of a new method, radically different from the two just compared. Our experience of nearly four years of varied work seems to indicate that the search for such method will not be an easy one. The many degrees of quantivalence of uranium and the unsuitable properties of its compounds combine to render the problem one of unusual difficulty. When face to face with a problem of this kind one cannot but admire the wisdom of Stas in selecting chiefly univalent elements with powerful affinities in order to prove the constancy of the atomic weights.

The result of our analyses of uranous bromide may be summed up in the following words:—If oxygen is taken as 16.000, and bromine as 79.955, the atomic weight of uranium appears to be not far from 238.53.

NOTICES OF BOOKS.

A Text-book of Inorganic Chemistry. By A. F. HOLLEMAN. Rendered into English by HERMON C. COOPER, with the co-operation of the Author. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1902. 8vo. viii.-458 pp. Ill.

THIS superior text-book made its first appearance in 1898 at Groningen, where the author holds a Chair in the University. Two years later a German translation was published, and has met with great success, having been adopted at the Universities of Würzburg, Freiburg, Munich, Breslau, Göttingen, Zürich, Vienna, St. Petersburg, Tokyo, and elsewhere. English and American students will welcome this translation, which has been carefully made by Dr. Cooper.

The distinctive features making this book a decided advance on its predecessors are tersely stated by the German reviewer of the edition that appeared in 1900. He wrote:—"The work combines the new achievements of physical chemistry with the mass of long-established facts of inorganic chemistry so as to form a unified whole." It will not be necessary hereafter for students to get acquainted with the common phenomena of elementary chemistry by the perusal of one book written on the old plan, and then to take up the independent study of the laws of physical chemistry (notably those established by van't Hoff, Ostwald, and Arrhenius, and their disciples), as set forth in some other manual devoted to that subject. He will find that Holleman combines all these points in one volume. Sections on osmotic pressure and its relation to molecular weights, on dissociation, electrolytic dissociation, thermo-chemistry, methods of determining atomic weights, the periodic system, and electro-chemistry, all in their most modern aspects, are introduced at intervals among purely descriptive and didactic pages, so naturally that they seem to make a part of the science, and not independent theories invented for the amusement of their authors and their friends.

At the same time the descriptive matter is most judiciously selected, and the theoretical views are introduced at such points that they can be illustrated and explained by the matters under consideration, thus presenting a harmonious view of the science. The theories

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy of Arts and Sciences*, xxxvii., No. 14.

are treated on a mathematical basis, but the calculus is used very sparingly.

Without prejudice, the names of persons to whom credit is due are mentioned in connection with their work. The Americans, Gibbs, Clarke, Morley, Saunders, receive notice alongside of the Europeans, van 't Hoff, Arrhenius, Ostwald, Nernst, Berthelot, and others.

The translation is satisfactory and generally free from ambiguity. On page 289, however, near the bottom, the discovery of germanium is said to have been made by the chemist who named an unknown element "ekasilicon," owing to the misuse of a pronoun. The proof-reading shows great care, but on page 275, in the table, for "Sp. G." read "Sp. H." The expression "spectrum analysis" is preferred by the reviewer to "spectral analysis."

The author is to be congratulated on having written a capital text-book, so fresh in its treatment, so entirely up-to-date in matter, so accurate, and so utilitarian as to place it far above any work having the same objects in view that has appeared during the last twenty-five years. If we are not mistaken in our estimate, Holleman's "Inorganic Chemistry" will prove an epoch-making text-book.

There is a good index.

The same publishers promise a translation of Holleman's "Organic Chemistry," prepared by Drs. Walker and Mott, of Derby. H. C. B.

August Wilhelm von Hofmann; Ein Lebensbild. By JACOB VOLHARD and EMIL FISCHER. Berlin: R. Friedlander und Sohn. 1902.

The work of preparing a biography of Hofmann was originally entrusted by the German Chemical Society to Ferdinand Tiemann and Emil Fischer. On the premature death of the former, however, Jacob Volhard undertook his portion of the task. This book, the outcome of the joint labours of the pupil and successor of Hofmann, is divided into two parts. The first is purely personal and social, and gives us a delightful picture of Hofmann, the man; many of his letters to members of his family are inserted in full, and it is easy to trace in them the characteristics which marked him out as a most successful author. The simple, ingenuous, and yet acute nature of the great chemist is laid bare before us, his domestic joys and sorrows, and his dealings with the College of Chemistry, which in its early years encountered so many difficulties from which it finally emerged under Hofmann's skilful guidance. Some of the letters written from Osborne, whither he went by Royal Command to lecture before the Queen after the death of the Prince Consort, display an extraordinarily vivid sense of humour, and it is difficult to resist lingering over this portion of the book, which is fascinating reading for all who can appreciate a good biography.

The second part, written by Emil Fischer, is devoted to Hofmann's scientific work. Here, owing to his enormous activity, the summariser's task has been by no means easy. His extensive work upon aniline, and organic nitrogen compounds generally, his influence on the coal-tar colour industry, his work on the aliphatic mustard oils, to mention only a few examples, are all described as fully as space permits, and all will agree with the author that he was the greatest of Liebig's pupils, and that his name may well be coupled with those of the heroes of German Chemistry. The whole book gives us a vivid picture of a delightful man, an inspiring teacher, and an extraordinarily able and successful investigator.

Beiträge zur Chemischen Physiologie und Pathologie. Edited by FRANZ HOFMEISTER. Band II., Heft 4. Braunschweig: Friedrich Vieweg und Sohn. 1902.

This short number of the *Beiträge* includes a paper by Dr. Ernst Fuld on the compounds of albuminous bodies with metaphosphoric acid. Without committing himself

to a definite statement, the author conjectures that, for serum albumen, from the percentage of phosphorus in the metaphosphoric acid compounds, a molecular weight of 5590 may be assumed for the phosphate and 5100 for the pure albumen. The latter number agrees closely with the lowest obtained from the percentage of sulphur. Another paper, occupying a considerable part of the number, deals with the curdling effect of rennet upon milk, examined both from a theoretical and practical standpoint. In a short communication on a modification of Kjeldahl's method of determining nitrogen in organic substances, the use of sodium thiosulphate is advocated to decompose the amido-mercury salts formed on addition of mercuric oxide. Commercial thiosulphate is said to be free from nitrogen, and has the advantage of being able to be used in the solid state, whereas alkali sulphides have to be employed in aqueous solution, thus inconveniently increasing the volume of liquid to be distilled, and lengthening the process.

Handbook of Technical Gas Analysis. By CLEMENS WINKLER, Ph.D., Professor of Chemistry at the Freiberg Mining Academy. Second English Edition. Translated from the Third, greatly enlarged, German Edition, with some Additions, by GEORGE LUNGE, Ph.D. London: Gurney and Jackson. 1902. Pp. 190.

The third German edition of this book was published in 1901, and as the first English edition was just exhausted, the proof-sheets of the former were kindly lent to the translator for the preparation of this second English edition. The book has been considerably enlarged, the number of pages having been increased by one-half, though the scope of the work remains the same. Even now all the processes and apparatus proposed for gas analysis are not included, but only the most important of them, including the valuable additions to technical analysis made by Prof. Hempel.

Gas analysis is usually effected by measuring and not by weighing, and for the most part the results are given in parts per cent, or per 10,000 by volume, which volume must be corrected for pressure and temperature.

The analytical process followed in the examination of gases generally consists in transforming one constituent after the other into a compound of a different form. From the contraction of volume thus produced, the volume of each special constituent can be deduced, directly or indirectly. This can be done in three principal ways:—1. By direct absorption. 2. By combustion. 3. By combustion and subsequent absorption of the products. And, according to how the process is conducted, gases can be estimated either by direct measuring, by titration, or by weighing.

Chapters I. and II. are on taking samples of gases, and general remarks on their measurement; and Chapter III., which forms the principal part of the book, deals with the apparatus and methods for carrying out the analysis of gases. This chapter is divided into three principal subdivisions on—the estimation of solid and liquid admixtures, the estimation of gases by absorption, and the estimation of gases by combustion; and in every case the method and procedure are fully and clearly described, while an important feature of the book is the illustrations, which are numerous and excellent. The appendix contains a number of tables indispensable for working out results, and, finally, there is an index.

Les Combustibles; Solides, Liquides, Gazeux. ("Fuels; Solid, Liquid, and Gaseous"). By H. J. PHILLIPS, F.I.C., F.C.S. Translated from the Third English Edition by J. ROSSET. Paris: Gautier-Villars. 1902. Pp. 165.

FUELS are at the base of almost all industries, whether by transforming their heat of combustion into mechanical energy—as in steam, petroleum, or gas engines—or for transforming natural products into commercial materials,

as in metallurgy. In every case it is important to know the exact value of the fuel used; and this value depends not only on its calorific power, but also on its chemical composition. The presence of sulphur, phosphorus, &c., in fuels makes them useless for certain purposes, so an exact analysis is of importance.

The scope of this book is to give the simplest methods for the analysis of solid, liquid, and gaseous fuels, as well as the methods for the determination of their calorific power.

At the end of the book is a series of tables giving the composition and calorific power of all kinds of commercial fuels, such as coal, coke, petroleum, and furnace gases from both regenerative and blast furnaces.

The references in the index do not seem to be as simple as they might. Instead of giving the number of the page, the chapter and number of the paragraph are given. Thus:—Anthracite, VII., 4; VII., 24; Hydrogen (estimation of), II., 22; Oxide of iron, VI., 5; &c.

CORRESPONDENCE.

SCHRÖTTER'S CARBONIC ACID APPARATUS.

To the Editor of the Chemical News.

SIR,—I have recently performed a number of analyses of baking powder, and as I found the usual form of Schrötter's CO₂ apparatus extremely difficult to clean, and more especially to dry, I have designed a modification which may be useful to some of your readers.

The ordinary tap-funnel and drying tubes of a Schrötter are sealed into a tube, which is then accurately ground into a weighing bottle in place of the stopper. If the long tube form of tap-funnel is used, that joint must be an inserted joint. The ground joint must be well made. This apparatus is, of course, very easy to clean and dry, while it is as accurate as the older form.

My model was made by Messrs. C. E. Muller and Co., of High Holborn, and I believe that they intend to stock it. I am, &c.,

C. E. KENNETH MEES.

The Chemical Laboratory,
University College, W.C., May 13, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 17, April 28, 1902.

Researches on Electric Piles formed by the Reciprocal Action of Oxidising and Reducing Liquids. Common Solvents. Action of Acids on Bases.—M. Berthelot.—The author performs a certain number of synthetic experiments, in order to show the order of chemical reaction susceptible of being produced under normal conditions in the midst of the tissues of living beings. He succeeds in liberating the acids, even the most energetic of them, such as hydrochloric and sulphuric, by electrolysis—acids whose existence is established either amongst the secretions of the stomach or on the surface of the organs.

Composition of Hydrate of Chlorine.—M. de Forcrand.—The composition of hydrate of chlorine has been much discussed. Faraday prepared this substance by desiccation of the crystals in the cold, and published a number of analyses, of which the mean gives as a formula

Cl₂+11H₂O. M. Roozeboom, using the same method, found 28.1 to 31.9 per cent of chlorine, and he believed the hydrate to have the constitution Cl₂+6H₂O. By two general methods, already described by the author, he finally solves the question of the composition, and finds it to be Cl₂+7H₂O.

Some Derivatives of Oxyisopropylphosphinic Acid.

—C. Marie.—Oxyisopropylphosphinic acid gives two series of salts, the neutral salts and the acid salts. He prepared the following:—Sodium salts: (a) neutral salt—PO₃HNa₂(C₃H₇O), 5H₂O; (b) acid salt—PO₃H₂Na(C₃H₇O), 6H₂O. Lead salt: PO₃HPb(C₃H₇O).

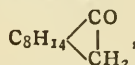
Copper salts: (a) acid salt—PO₂H₂^{Cu} C₃H₇O; (b) neutral salt—PO₃HCu, C₃H₇O, H₂O. Silver salt: PO₃HAg₂, C₃H₇O

Bulletin de la Société Chimique de Paris.

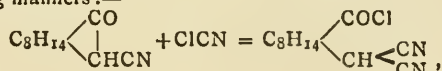
Series 3, Vol. xxv., Nos. 22.

Integral Method for the Destruction of Organic Matters, applicable to the Search for Mineral Poisons, especially Arsenic and Antimony.—G. Denigès.—Already inserted in full (vol. lxxxv., p. 26).

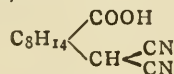
Particular Action of Chloride of Cyanogen on Soda-Camphor.—H. Duval.—While attempting to prepare cyanised camphor by the action of chloride of cyanogen on soda-camphor in solution in toluene, the author obtained a body which could not be identified either with the sought for product or any other known substance. After the passage of the chloride of cyanogen, the toluenic solution was extracted with weak soda. This latter solution, treated with an acid, gave a small quantity of a yellow coloured amorphous body; the return, however, was only 3 per cent. To crystallise this product, ether, benzene, and water were successively tried. The ether left a gummy mass; in benzene it crystallised in deep yellow-coloured flakes; with water almost colourless needles were obtained by the first crystallisation. Analysis showed that this substance contained nothing but carbon, hydrogen, and nitrogen. It is soluble in alkalis and easily displaces carbonic acid in the carbonates when heated; it may be, therefore, a carboxylised compound. As for its formula, if camphor be taken as—



we can see that the new body ought to contain two atoms of nitrogen and one carboxylised function; on the other hand, the method used warrants the supposition that a fresh molecule of the halogenised derivative has reacted on the cyanised camphor formed, in one of the two following manners:—



and that in both cases the potash has caused, by substitution or by scission, the formation of the substance—



The figures found by analysis give us:—

	Found.	Calculated for C ₈ H ₁₄ $\begin{array}{c} \diagup \text{CO}_2\text{H} \\ \\ \diagdown \text{CH} \begin{array}{c} \diagup \text{CN} \\ \diagdown \text{CN} \end{array} \end{array}$
N	13.04	12.72
C	65.24	65.45
H	7.34	7.22
O (by diff.) .. .	14.38	14.54

The Mechanism of the Etherification of Plants.—MM. Charabot and A. Hebert.—Already noticed.

The Agricultural Value of the Nitrogen in the Black Material of the Phosphates from the Pyrenees.—J. Joffre.—Already inserted in full.

MISCELLANEOUS.

The Andrew Carnegie Research Scholarships.—The Andrew Carnegie Gold Medal for 1902 has been awarded by the Council of the Iron and Steel Institute to Dr. J. A. Mathews, of New York, for the research carried out by him as a holder of an Andrew Carnegie Research Scholarship during the past year. The medal has been designed by Mr. G. W. de Saulles, of the Royal Mint. The first recipient, Dr. Mathews, has previously received a Fellowship for the encouragement of scientific research from Columbia College, New York, where he has been working under the guidance of Professor H. M. Howe. For the present year the Council of the Iron and Steel Institute has awarded six Andrew Carnegie Research Scholarships each of the value of £100. The following are some particulars of the careers of the successful candidates:—

Octave Boudouard, of Paris, aged 30, has already published thirty-two original memoirs, and, in conjunction with Professor Le Chatelier, four books. He is Assistant Professor of Chemistry at the College of France, and has previously received in France bronze and silver medals for research.

William Campbell, of New York, aged 25, has published papers for the Institution of Mechanical Engineers, the American Chemical Society, and the Franklin Institute. He studied at the Durham College of Science, and was awarded an 1851 Royal Exhibition Scholarship to the Royal School of Mines, London. He is now working under Professor H. M. Howe at Columbia College.

Alfred Campion, of Cooper's Hill, aged 27, is a member of the Iron and Steel Institute, who has had practical experience with the Steel Company of Scotland, and has previously written papers for Glasgow Societies.

Percy Longmuir, of Manchester, aged 25, was a student of the Sheffield University College. He has had experience in foundry work, and has written several papers on that subject.

Ernest Schott, of Berlin, aged 26, studied under Professor Ledebur, of Freiberg, and is Assistant in the Royal Testing Institution at Charlottenburg. He has published a number of original memoirs.

Frederick Henry Wigham, of Wakefield, aged 32, is a member of the Iron and Steel Institute. He is Steel Works Manager to Messrs. George Cradock, and Co., and communicated, in conjunction with Mr. Stead, a paper on steel for wire-making to the Iron and Steel Institute last year.

The Substitutions of Elements of the Sulphur-selenium-tellurium Group.—J. Krafft and O. Steiner.—If we heat selenide of phenyl, $(C_6H_5)_2Se$, in an open beaker with its equivalent quantity of sulphur, going nearly to boiling-point, the selenium is almost entirely displaced, and we obtain sulphide of phenyl, $(C_6H_5)_2S$. We can also operate at 300° in a sealed tube filled with CO_2 ; the selenium is deposited in the metallic state, and if we take up with ether, to dissolve the sulphide formed, we find that 95 per cent of the sulphur has displaced the corresponding quantity of selenium. Similar results are obtained by the action of sulphur on telluride of phenyl, $(C_6H_5)_2Te$, but it is necessary to operate at 280° in a sealed tube; after heating for ten hours 58 per cent of the tellurium is displaced, bisulphide of phenyl, $(C_6H_5)_2S_2$, rather than monosulphide, is formed. As for oxygen, it

does not act on sulphide of phenyl, but inversely sulphur acts slightly on oxide of phenyl, $(C_6H_5)_2O$; after heating for fifteen hours at 340° , a small amount of sulphide is formed, and many products of alteration. Sulphur heated to 110° in a sealed tube with selenious anhydride gives a selenium of the black variety, and sulphurous anhydride, which is liquefied. When heated to 55° with crystallised selenic acid, the sulphur is oxidised to the state of sulphuric acid, and causes the formation of selenium and selenious acid. Inversely, chloride of sulphur is decomposed by selenium and tellurium; the chloride of selenium, $SeCl_2$, decomposes on distillation into $SeCl_4$ and Se. In the case of tellurium, the chloride formed by the following equation can be isolated by distillation without decomposition:— $S_2Cl_2 + Te = TeCl_2 + 2S$. When sulphobenzide, $C_6H_5 \cdot SO_2 \cdot C_6H_5$, is distilled with selenium or tellurium, we obtain the selenide or telluride of phenyl, and at the same time SO_2 .—*Berichte*, vol. xxxiv., p. 560.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "The Laws of Heredity, with special reference to Man," by Prof. Carl Pearson, M.A., F.R.S.

— Society of Arts, 8. "Pageantry and the Masque," by Miss May Morris.

WEDNESDAY, 28th.—Chemical, 5.30. "Taxin," by T. E. Thorpe and G. Stubbs. "Soil Samples" and "Some Excessively Saline Indian Well Waters," by J. W. Leather.

THURSDAY, 29th.—Royal Institution, 3. "Contemporary British Sculpture," by M. H. Spielmann.

— Society of Arts, 4.30. "Western Australia—its Progress and Resources," by the Hon. H. W. Venn.

FRIDAY, 30th.—Royal Institution, 9. "The Progress of Electric Space Telegraphy," by G. Marconi, M.Inst.E.E.

SATURDAY, 31st.—Royal Institution, 3. "The Development of the English Drama—I., The Drama of the Middle Ages," by Prof. Brander Matthews, Litt.D., D.C.L.

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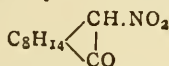
VOL. LXXXV., No. 2218.

THE CONDITIONS DETERMINATIVE OF CHEMICAL CHANGE AND OF ELECTRICAL CONDUCTION IN GASES, AND ON THE PHENOMENA OF LUMINOSITY.*

By HENRY E. ARMSTRONG, V.P.R.S.

(Concluded from p. 243).

In a case like that of radium, it would seem that energy of low period suffices to bring about the change the reversal of which subsequently gives rise to the luminous effect and radio-activity. The chemist is tempted to contrast the behaviour of radium with that of a substance undergoing change into an isodynamic form—such as nitro-camphor, for example. Nitro-camphor—



dissolves readily in alkalis, but its salts are derived from a pseudonitro-camphor, the group CH.NO_2 undergoing alteration into the group C(NO.OH) . When liberated from its salts, the pseudo-form at once, in great part, reverts to the normal form; on the other hand, when solid nitro-camphor, which apparently consists almost entirely of the normal form, is dissolved in a liquid, it in part gradually undergoes conversion into the pseudo-form. A point of equilibrium is eventually reached when from 7 to 10 per cent of the pseudo-form is present (compare Lowry, *Chem. Soc. Trans.*, 1898, p. 966). The change proceeds at different rates in different solvents, and is undoubtedly conditioned by some catalyst; in other words, either form of the pure substance would be stable. It will be apparent that the change is one which does not affect the molecule as a whole, but merely an isolated region in it. If the energy set free in the formation of the dominant form were of sufficiently high period, nitro-camphor might appear luminous and even be radio-active. The argument is of interest, as it serves to suggest that radio-activity may not be the isolated phenomenon we at present suppose, but a concomitant of many chemical changes.

[From this point of view, it appeared to be desirable to examine substances such as saccharin (orthobenzoic sulphuride) and cane-sugar, which glow in a very remarkable manner when broken up. Mr. E. W. Lewis has kindly made a number of experiments for me, but without obtaining positive results; although an intense photographic impression of the flash is easily obtained by merely crushing crystals of saccharin or sugar on a glass plate held above a sensitive film, crystals placed on a film are without effect, even when left in contact with it during several days. It will, however, be desirable to apply the far more delicate electroscopic test to such substances under various conditions. It so happens that the property referred to was first noticed in the case of saccharin in my laboratory (in 1895) by Mr. Jackson Pope (*Chem. Soc. Trans.*, 1895, p. 985), and in March last I applied to this gentleman for a specimen of the substance he had prepared in 1895. He was able to send me crystals, but informed me that those he had tested were inactive. We found this to be true of the remainder, at most a very feeble glow being observed on crushing them; but active crystals were obtained on re-crystallising the inactive material from acetone. Old specimens of sugar crystals appear to be as active as new ones.—*Note, added May 2*].

A class of effects attendant on radio-activity, and which have an important bearing on the question previously considered, are those attributed to emanations from radio-active substances. Sir William Crookes has brought the subject prominently under notice in his recent communication. The behaviour of such emanations is strikingly similar to that of ordinary gross matter; indeed, it is difficult to resist the conclusion that such is their character, and that they are but secondary products engendered by radio activity.

[Professor Rutherford's recent observations on the "emanation" from thorium compounds are very difficult to interpret. The assumption that Mr. Soddy and he are inclined to make (*Chem. Soc. Trans.*, 1902, p. 321), that the emanation is allied in properties to the elements of the argon group, is almost a contradiction in terms. Such a constituent would presumably be an inert substance, and if not removed by the drastic treatment to which they submitted their material without permanently affecting its radiation power, it would scarcely then escape spontaneously on mere exposure of the solid. It would seem to be far more probable that the "emanation" is a secondary manipulation, in some way conditioned by the "straight-line radiation."

There is a feature in Dr. Russell's experiments which has always struck me as remarkable, assuming that the photographic effects he has obtained are due to hydrogen peroxide, viz., the absolute sharpness of the images formed by a scratched zinc plate, even when this is placed at a relatively considerable distance above the sensitive film. If the emanation passed by mere diffusion from the active surface, a more or less blurred image might be expected to form. It would almost seem that the molecules are projected in straight lines—in other words, that they may be electrically charged. If so, a distinction should perhaps be drawn between a merely vapourised substance and a "nascent" substance.—*Note, added May 2*].

The production of hydrogen peroxide under such an influence at once presents itself not merely as a possibility, but practically as a necessity. There is every reason to suppose that hydrogen peroxide is a necessary product of oxidation by ordinary oxygen whatever the substance oxidised; but the conditions under which it is produced are usually such as to engender its own immediate decomposition—so that it either escapes observation or is met with only in minute quantity. The oxidation of zinc may be taken as an example. The oxidation necessarily takes place in a circuit comprising (a) the impure metal—which because it is impure furnishes both negative and positive electrode—(b) conducting (impure or dirty) water, and (c) oxygen, of which the last acts as depolariser. The water is electrolysed, its oxygen going to the metal; at the same time, the hydrogen from the water becomes associated with the depolarising oxygen molecule, forming hydrogen peroxide, H_2O_2 : the products, in fact, are zinc oxide and hydrogen peroxide in equivalent quantities, not merely zinc oxide as is taught by the text-books.

It does not seem to me that Sir William Crookes has disproved the possibility that the effects may be due to hydrogen peroxide by his experiment in which one limb of a U-tube passed through the cork in a bottle containing a solution of the peroxide, the open end of the other limb being put close to a sensitive film, the result being that no photographic effect was observed in seventy-two hours, although a strong effect was produced when the film was kept over the mouth of the bottle during only twenty-four hours. The peroxide molecules would undoubtedly tend towards the walls of the tube, especially at the bend; but collision therewith would probably have fatal effects, as the alkaline surface of the glass would promote their destruction.

The argument may be applied to recent researches on the so called ionisation of air and other gases. If this term implied the recognition of nothing more than the power of conducting, little difficulty would arise. Faraday, with characteristic and truly scientific caution, used the

* A Paper read before the Royal Society, May 1, 1902.

word *ions* simply "to express those bodies which can pass to the electrodes." Unfortunately, of late years the signification of the word has been entirely altered: ionisation now connotes a schism—a process of molecular suicide; and the ions are looked upon as discrete particles enjoying separate existence, as the electrically charged, wandering elements of molecular disruption. Before we assume that such ions are present in air under ordinary conditions, and that they alone can condition conductivity, it behoves us to examine carefully into the nature of the evidence which is relied on in proof of their presence. It appears to me that much of the work done in this field is open to criticism. Thus, in Mr. C. T. R. Wilson's experiments (*Roy. Soc. Proc.*, 1901, vol. lxxviii., p. 151; vol. lxxix., p. 277), even the minute amount of chemical change occurring at the surface of the sulphur bead attaching the gold leaf of the electroscope to its support, may have sufficed to render the atmosphere within the flask conducting. And in the later experiments of the same observer, the phosphoric anhydride used as drying agent may have contributed an acid impurity. Sir William Crookes has recently given an illustration of the manner in which impurities may be derived from phosphoric anhydride. By heating it strongly *in vacuo*, he got rid of these to such an extent that they were no longer recognisable by the spectroscopy; but it cannot be supposed that even such treatment suffices to render the anhydride innocuous, bearing in mind the extraordinary delicacy of the electroscopic test.

I venture to think that until the phenomena of conductivity presented by gases have been studied not merely with the same, but even with far greater, care than has been devoted to the study of those attending gross chemical changes in gases, it is premature to conclude that gases undergo ionisation—using the word in its modern sense. I also venture to think that the question whether mere molecules cannot form conducting systems has not yet received in any way the attention it deserves from those engaged in these inquiries.

HISTORY OF THE INVENTION OF INCANDESCENT GAS-LIGHTING.

By AUER VON WELSBACH.

IN the year 1830 I was occupied with the chemistry of the rare earths. The remarkable phenomena exhibited by some of these earths, when heated to a high temperature by a flame, excited my interest to a great extent. One body in particular, called *erbia* by chemists, behaved in an altogether singular manner. It did not become luminous like other bodies and give off white or yellow light, but its radiations were green. Science has not yet been able to give any explanation of this remarkable phenomenon. This fact, which was interesting and astonishing to the highest degree, may be compared with the observations recently made on the radiations from polonium, for example.

I refer to this phenomenon because it interested me very greatly, and was, so to speak, the starting-point of my discovery. The spectrum given by this earth is not continuous; it is a band spectrum such as is given by but few solid bodies.

The examination of the light emitted by the rare earths raised to incandescence was very important in the study of these compounds. But the little beads easily obtained on platinum wires are not suitable for the production of very luminous spectra. I therefore arranged the earths in the flame in such a manner that the emission of light should be much more intense. It occurred to me, quite by chance, to soak cotton with the solutions of the salts of these earths, and then to calcine them. It seemed probable that this experiment might not succeed, and that the skeleton formed by the earths, after the combustion of

the cotton, would not have sufficient coherence. However, it was a success; the earths retained the shape of the cotton. Shortly afterwards, when I visited my old master, Bunsen, at Heidelberg, and explained to him how I had manipulated these compounds, he shook his head and said that it seemed impossible to him that a coherent mass of oxide could be obtained in that manner. I still remember with pleasure the astonishment he evinced when I was able to show him how I obtained my mantles.

During the course of my experiments to give these earths a structure appropriate for their luminous emissions, I came across one substance of which the very considerable emissive power was then but little known, for the reason, as I have stated, that these bodies had only been examined in the form of small beads. This compound was oxide of lanthanum, and it is this substance that gave me the idea of utilising the rare earths for the production of light on the large scale.

The mantle of oxide of lanthanum seemed perfect, but in it I found my first disappointment. I was away from the laboratory for several days, but had left the mantle carefully locked up; when I returned it was reduced to powder. I repeated the experiment with the same result. Oxide of lanthanum was always reduced to fine powder. My first joy was of short duration.

Then I began to think whether I could make oxide of lanthanum, whose emissive properties I was so absolutely certain of, more stable by mixing it with a compound which would attract the moisture and the carbonic acid of the air less easily. I experimented first on magnesia. I was already aware of the importance of the extreme division and the intimate mixture of the material to be calcined. The pulverisation ought to be integral, and I named these mixtures molecular mixtures. When we mix these bodies in this manner and calcine them, their properties undergo important modifications. White magnesia and white oxide of lanthanum, on being calcined, give a substance of a deep brown colour, and the properties of the compounds can be no longer recognised in the product. The first satisfactory compound for incandescent lighting with gas was formed of the oxides of lanthanum and magnesium. It did not fall to powder in the air after calcination, and it gave a beautiful light; however, its useful effect was not yet very great, it was just about that of a Siemens regenerating burner. But it had one great fault: after seventy or eighty hours of heating it became translucent and vitreous, losing its porosity. Thus, finally, this second attempt did not succeed.

I studied this question anew, from the chemical point of view; it was evident that magnesia did not resist fire sufficiently, that it could not undergo a prolonged calcination without being considerably modified. So I turned my attention to mixtures having oxide of zirconium as a basis. The results obtained were better. This mixture gave a steady light, and its life in the flame reached some hundreds of hours; this success gave me further encouragement, and at the same time I made experiments with oxide of thorium, and was surprised at the intense increase in luminosity of the mixtures containing this substance. These experiments showed that certain molecular mixtures of oxides constituted alloys, so to speak, which emitted a particularly intense and constant light when placed round a flame in the form of a fine net-work.

I already looked upon it as a certain fact that a new system of lighting could be founded on these phenomena, more economical and advantageous than the use of gas in the form of ordinary light-giving flames.

It must, however, be remembered—and this is the key to the invention of gas-lighting by incandescence—that the question was not to find a process by which an infusible compound could be given a definite shape. This invention is founded, above all, on the fact, proved by numerous experiments, that molecular mixtures of certain oxides are possessed of properties which cannot be deduced from those of their constituents,

Encouraged by all these results, and sustained by my experiments, I was bold enough to look upon the efforts made for the previous ten years to augment the lighting power of the gas-flame as useless. It is, in fact, evident that, the emissive power of these compounds being double or treble that of the simple flame with an equal consumption of gas, it is more economical to give up the use of a luminous flame. It is far better to use a non-luminous very hot flame to raise these new bodies to incandescence.

I now come to some well-known facts. I gave a small demonstration to the Viennese press in the laboratory of M. Lieben, and the reports, which were for the most part favourable, announced my invention to the public. While some looked upon this invention with approval, others affected a good deal of scepticism, or made fun of it. I am acquainted with a well-known gas engineer who was always ready to bet with any one he met, that less than 1000 burners a year would be installed in any town. Another one, when asked to interest himself in the new invention, said:—"In my works we only take notice of serious ideas."

These answers did not affect my confidence. Incandescence by gas was welcomed, and gradually gave rise to a certain amount of business. I was obliged to leave this subject for some time, my attention being occupied by contracts and other matters. For the purpose of continuing this work I found a very distinguished man who rapidly set about the manufacture of the "lighting fluid," as we named it. This was M. L. Haitinger, whose work on this subject must not be forgotten, and to whom I owe most hearty thanks.

He soon made the interesting observation that the compounds of cerium, which were present in small quantities in the material, were of great importance with regard to the emissive power, and that under certain conditions it was very advantageous to increase the proportion of cerium. He submitted all the mixtures to very exact analysis, and could thus make sure of a good preparation. Eventually I returned to this work and made some hundreds of experiments, without great success, to increase the luminosity of the mixtures. The industry of incandescent gas-lighting was in difficulties, and a continuous sort of stagnation set in; those who had doubted in the beginning again raised their voices, and a very painful time passed for me. Capitalists, mistaken in their hopes, became impatient, and instead of giving me time and leaving me to work quietly, threatened me with legal proceedings. The factory constructed some years before at Atzgersdorf was closed down, and its staff of chemists departed to the four quarters of the globe; finally, I took possession of it and remained there alone.

"Necessity is the mother of invention." It was necessary to achieve something. I started fresh experiments on all possible bodies, but in vain; incandescence by gas did not appear to be susceptible of improvement.

At the commencement of my experiments I had, as I have said, directed my attention to oxide of thorium, and I had observed that it excited the emissive power of other earths. The light given by mixtures having a thorium base was intense, but it did not last. It decreased after about fifty or sixty hours, and was no better then than that from mantles not containing thorium. This astonishing fact made me think that thorium had not yet been examined with sufficient care from the scientific point of view; that is to say, that it contained some substance hitherto unknown to chemists. There chanced to be in the stores at the Atzgersdorf factory a certain quantity of raw, impure thorina. I set myself to work examining this substance, which was then very rare and expensive. I soon found several chemical methods for treating this compound in a much more simple fashion than it had been done before; among others those methods of crystallisation which enabled me rapidly to prepare the pure salts of thorium. A curious fact was then observed, the purer the thorium the less intense was the light given by the mantle made from it. I followed up these experiments, and finally

obtained a mantle which only gave a light of two candle power, and I convinced myself by a careful analysis that the thorium which composed it was purer than any of my other preparations. From this I concluded, perhaps a little hastily, that thorium was not an element, but that it could be decomposed. The examination of the mother-liquors showed that they contained the real luminous substance. The decomposition thus seemed to be apparent, but in the mother-liquors from the purest portions I could not find any foreign body. Subsequent experiments, however, enabled me to prove the existence of this luminous compound.

This body, closely allied from many points of view with thorium, and of which the salts were entangled by the salts of thorium, although they were not isomorphous—this body was cerium. The synthesis of the mother-liquors was a simple task; I gradually mixed a solution of cerium with a solution of pure thorium, and I obtained the astonishing light that everyone now knows. The emissive power of the new mixture was about three times that of the old; its life was also much longer, and it opened a new era for incandescent lighting by gas. I made this experiment with the greatest care; I measured the resistance to the action of the air and of the flame; and the decrease in the illuminating power, and at the beginning of the year 1890 I again brought incandescent gas-lighting before the public.

As a general rule the mantles have been kept to this last composition; that is to say, 99 per cent of oxide of thorium and 1 per cent of oxide of cerium.

The value of my patents had then fallen to a minimum, and it was high time that these new results were achieved if I did not want to lose the last few faithful friends who remained to me. Among these I may mention the firm of Julius Pintsch, of Berlin, who were also the first to replace the woven by the knitted mantles, an important improvement I had forgotten to mention.

From the development of incandescent gas-lighting, as I have just described it, it can be seen that my work was not based upon that of others.

When incandescent gas-lighting had arrived at this point the era of lawsuits commenced. Numerous persons, after having rummaged old volumes to find something analogous, came and told me a number of things and names I had never heard mentioned before. I maintain that incandescent gas-lighting was born at Vienna, and that neither I nor my collaborators have ever used the inventions of other people, and I think I have given the best proof of this by what I have said above.

As for this singular property which is possessed by this mixture of 99 per cent of oxide of thorium and 1 per cent of oxide of cerium, it can be seen, it can be observed, but it cannot be explained. This powerful emissive property cannot be foreseen from any property of thorium; this latter hardly possesses it. We can give no exact scientific reason for this excitation of emissive power by cerium, and I expect we shall have to wait a long time before it is explained.

I myself can give no explanation, but I can point out certain analogous facts. These are only ideas, and are not absolutely based on experiments, but still I should like to refer to them briefly.

A body having this emissive power, that is to say, susceptible of emitting an intense light when raised to incandescence in a flame, is composed of infusible oxides in molecular mixture. The principal constituent of this mixture should remain intact in the flame, while the other may be easily reduced and oxidised.

The ponderable relationship between the elements in the mixture should depend on the pressure at which we operate; at the atmospheric pressure this relation is 1 of cerium to 99 of thorium; it might be much more at a pressure of 100 atmospheres.

The gas of the flame successively and very rapidly oxidises and reduces the emissive substance at the points where it is situated in the mantle. If the constituents of the mixture

could form a compound when one of them is in a state of higher or lower oxidation, the compound would be quickly destroyed at the moment when the body concerned passes from the usual to the other degree of oxidation. The earths are in a state of extremely fine division, and are surrounded by a mantle of flame both oxidising and reducing. If reduction takes place there is also decomposition, and if oxidation there is re-combination of these elements; these reactions may go on several million times a second, and molecular shocks are produced which give rise to luminous oscillations of the ether, and the body becomes incandescent.

We may make use of all the substances formed according to this general principle, and for a low consumption of gas they give an intense light. When we examine the whole series of these bodies, of which M. Haitinger has found some, we find another peculiarity which the oxides in the form of salts give to emissive mixtures. These bodies are not chemically but physically analogous; in a certain sense they are isomorphous; that is to say, they crystallise together and form special double salts; the double salts of cerium and thorium are an example. Among the bodies having this emissive power when calcined in molecular mixture we may mention alumina and oxide of chromium. These bodies behave like the oxides of thorium and cerium, only their emissive power is very much less. Oxide of chromium plays the part of the easily oxidisable and reducible oxide, and the alumina that of the infusible basis.

Oxide of chromium and alumina, chromium and aluminium, are not very closely allied from the chemical point of view, still they combine, and each form a series of isomorphous double salts, the alums. Another example is the excitation of this emissive power in lime and strontia by uranium, another discovery of M. Haitinger's.

Small quantities of uranium have the same effect on oxide of thorium. With lime the emissive power of this mixture is very considerable, and for some time we thought of applying it commercially. There again we see the same relations appear. The lime is the infusible basis and the oxide of uranium is the easily reduced and oxidised body. Although these two elements are not closely allied chemically they form certain compounds, of which uranocalcite, which is found in nature, is an example. Their oxides, like their salts, can combine and separate according to the degree of oxidation of the oxide in question. I do not know whether my hypothesis will be acceptable. I have given it because many facts are in its favour, and I know of no observations which are opposed to it. Possibly, again, this explanation might help the development of incandescent gas-lighting.—*Ann. fur Gesbelucht. und Wasservers.*, 1901, p. 661.

The Solubility of Salts. The Sodium Salts of some Bibasic Acids analogous to Sulphuric Acid.—R. Funk.—This paper deals with the comparative solubilities of the neutral sulphate, chromate, molybdate, and tungstate of sodium in their different hydrated forms. All these salts will crystallise in water with 10 H₂O, or anhydrously; the molybdate and tungstate further crystallise with 2 H₂O. The curves of solubility of these salts show a remarkable parallelism. The following are a few of the results obtained at 18°:—

	Density of the saturated solutions.	Molecules of the salt per 100 mols. of water.
SO ₄ Na ₂ +10H ₂ O	1'140	2'1
SeO ₄ Na ₂ +10H ₂ O	1'315	3'9
WO ₄ Na ₂ +2H ₂ O	1'573	4'4
MoO ₄ Na ₂ +2H ₂ O	1'437	5'7
CrO ₄ Na ₂ +10H ₂ O	1'432	7'4

—*Berichte*, vol. xxxiii., p. 3696.

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS OF THE YTTRIUM GROUP.*

I.

By L. M. DENNIS and BENTON DALES.

Historical.

THE first of the rare earths was discovered by Gadolin (*Sv. Vet. Akad. Handl.*, 1794, p. 137; *Crell's Ann.*, 1796, I., 313), in 1794, in a heavy black mineral which had been found at Ytterby some six years before by Arrhenius. Three years later the earth was named yttria by Ekeberg (*Crell's Ann.*, 1799, ii., 63), and the mineral "yttristone." The latter is the gadolinite of the present day mineralogists. Ekeberg (*Sv. Vet. Akad. Handl.*, 1802, p. 68; *Ann. de Chim.*, xliii., 278) found yttria in a new mineral in which he had discovered tantalum, and which he called yttrantalite. The earth was further studied by Berzelius (*Schw. J.*, xvi., 404), and by Berlin (*Sv. Vet. Akad. Handl.*, 1835, pp. 209, 212; *Liebig's Ann. Chem.*, xxviii., 222), both of whom considered it homogeneous.

Scheerer (*Pogg. Ann.*, lvi., 482) observed that when yttria was heated strongly in an open vessel it took on a yellow colour, which it lost on heating in the presence of reducing gases, and that it remained colourless if cooled quickly, whereas it became coloured again if heated in contact with air. He thought this phenomenon due to the presence in the yttria of some other earth, perhaps new, perhaps lanthana, capable of forming easily a peroxide. His work was soon followed by the researches of Mosander (*Phil. Mag.*, xxiii., 251; *Liebig's Ann. Chem.*, xlviii., 219), who separated the old yttria into three new earths. He kept the name yttria for the most basic of these; the middle one he called terbia, and the least basic one erbia. His yttria was white, and gave colourless salts; terbia he thought to be white also, but it gave rose-coloured salts, while erbia was orange-yellow and gave colourless salts. He used the methods of fractional precipitation of the oxalates by oxalic acid from acid solution, and of the hydroxides by dilute ammonia, in both of which his erbia was thrown out first, then terbia, and lastly yttria. His results were confirmed by Berzelius ("Lehrbuch," 2nd French Edition, ii., 163), by Svanberg, and by Scheerer.

The earths of old yttria were re-examined in 1860 by Berlin (*Scand. Naturf. 8 Møde Kjöbenhavn*, 1860, p. 448). He was the first to use the classic method of fractional decomposition of the nitrates by heat. He obtained only two of Mosander's earths, the white yttria and the one giving rose-coloured salts, terbia, which he and all subsequent investigators have called erbia. Mosander's yellow erbia, the present-day terbia, he could not obtain.

Popp (*Liebig's Ann. Chem.*, cxxxi., 179) in 1864, and Delafontaine (*Arch. des Sci. Phys. et Nat.*, [2], xxi., 97; xxii., 30; xxv., 105; *Liebig's Ann. Chem.*, cxxxiv., 99; cxxxv., 188) in that year and the two following ones, working at this same problem, arrived at totally different conclusions. Popp, using both of Mosander's methods, could separate neither erbia nor terbia. He thought erbia a mixture of the cerite oxides, and terbia a mixture of erbia with yttria. Delafontaine maintained that these two earths existed. Mosander's erbia he obtained by fractional precipitation with primary potassium oxalate, the small amount of yttria and terbia being removed by treatment with potassium sulphate solution. To separate the terbia and yttria remaining, he fractionated again the least coloured oxalates, then dissolved out the yttria by repeated treatment with dilute acid.

Then Bahr and Bunsen (*Liebig's Ann. Chem.*, cxxxvii., 1) in 1866, using a modification of Berlin's method of fusion of the nitrates, corroborated Berlin's results. They obtained only the true or white yttria and the rose-coloured erbia of Berlin (Mosander's terbia). Cleve and Höglund (*Bull. Soc. Chim.*, [2], xviii., 193, 289) in 1872, using the same method, obtained the same result.

* *Journal of the American Chemical Society*, vol. xxiv., No. 5.

Until Mendeleeff's announcement of the periodicity of the elements (*Liebig's Ann. Chem.*, Suppl., viii., 133, esp. p. 184 ff.), yttria, ceria, and the other rare earths had been generally assumed to have the formula RO. He, however, showed that their properties placed them in the third group of his arrangement, where their maximum valence would be three (oxide, R_2O_3). Lanthana he considered to be RO_2 . In order to put them into this group, it was necessary to increase their accepted atomic weights by one-half. Cleve (*Bull. Soc. Chim.*, [2], xxi., 344) in 1874, published new researches upon the salts of yttria and erbia, which tended to show the correctness of Mendeleeff's view of the triatomicity of these earths. Nilson (*Ber. d. Chem. Ges.*, viii., 655; ix., 1056, 1142), working upon the selenites in 1875, and upon the chlor-platinum compounds in 1876, further strengthened the idea that the rare earths, lanthana included, were sesquioxides.

A great increase in activity in rare earth research occurred in 1878, when the mineral samarskite, found in large quantities in North America, became the source of the material.

Smith (*Proc. Acad. Nat. Sci. Phil.*, xxix., 194; *Comptes Rendus*, lxxvii., 146, 148) in 1877 isolated an earth which he considered to be new, or perhaps the third earth of Mosander. He thought it new because of the insolubility of its double potassium sulphate in saturated potassium sulphate solution. Marignac (*Arch. des Sci. Phys. et Nat.*, [2], lxiii., 172; *Comptes Rendus*, lxxvii., 281) showed this property to be only a relative one, and he deemed Smith's mosandria to be identical with terbia. Neither could he agree to Smith's other claim that mosandria was identical with Soret's X. Delafontaine (*Comptes Rendus*, lxxvii., 600) considered mosandria to be terbia. Considerably later (1886), Lecoq de Boisbaudran (*Comptes Rendus*, cii., 647), having obtained a sample of Smith's impure mosandria, found that it contained, besides didymia and samaria, gadolinia and terbia.

Delafontaine (*Arch. des Sci. Phys. et Nat.*, [2], lxi., 273; *Ann. Chim. Phys.*, [5], xiv., 238) and Marignac (*Arch. des Sci. Phys. et Nat.*, [2], lxi., 283; *Ann. Chim. Phys.*, [5], xiv., 247) settled the question as to the existence of terbia by preparing it. Delafontaine treated his yttria earth mixture in solution with a saturated solution of sodium sulphate containing crystals of the salt, then fractionated the precipitated portion with oxalic acid from strong nitric acid solution, and finally treated the first of these precipitates with formic acid and concentrated. Terbia crystallised out as formate. There was also a yellow earth in the portion soluble in the sodium sulphate, but it was not so deeply coloured as terbia, and gave besides a base of lower atomic weight. He thought it a new element. Marignac obtained terbia as well as yttria and erbia by fusion of the nitrates. By making several hundred fractions and by properly combining them he obtained finally pure yttria at one end and erbia at the other. The intermediate products possessed a yellow colour. These he combined and fractionated by oxalic acid in acid solution. Erbia and didymia he found to go with terbia. Didymia he removed by the potassium sulphate treatment, but he could not free his product from erbia. Hofmann and Krüss (*Zeit. Anorg. Chem.*, iv., 27) in 1893 studied terbia, and by fractionation with aniline hydrochloride succeeded in breaking it up into two probable earths with metal atomic weights of 148 to 150 and 160, calculated as R^{III} . In 1895 Lecoq de Boisbaudran (*Comptes Rendus*, cxxi., 709) called attention to an absorption band in his terbia material which could not belong to any known element. He called the one which gives it Z_3 . Its band was at λ 4877.

The new earth which Delafontaine suspected in the saturated sodium sulphate solution mentioned above, was announced by him (*Comptes Rendus*, lxxvii., 559) as philippia. It was characterised by a magnificent absorption band in the violet at λ 450. Soret (*Comptes Rendus*, lxxxix., 521) stated that philippia was identical with the earth X, which Cleve denied (*Comptes Rendus*, lxxxix.,

708). Delafontaine (*Comptes Rendus*, xc., 221) maintained that philippia, Soret's X, and Cleve's holmia were identical, which Cleve again denied. Delafontaine (*Arch. des Sci. Phys. et Nat.*, [3], iii., 246) then admitted that the absorption spectrum ascribed by him to philippia belonged to Soret's X, but maintained still the individuality of the former. Roscoe (*Ber. d. Chem. Ges.*, xv., 1274) in 1882, by fractional precipitation of the double potassium sulphates with potassium sulphate, and by fractionation of the first portions of these by the varying solubilities of the formates, could obtain no product whose metal had a constant atomic weight of 121 to 123, and he concluded that philippia was a mixture of terbia and yttria. Crookes (*Phil. Trans. Roy. Soc.*, clxxiv., 910) agreed with Roscoe as to the non-existence of philippia. In 1897, Delafontaine (*Chem. News*, lxxv., 229) gave the methods by which philippia might be prepared; they were the standard ones of fractional precipitation of the nitrate solution of the rare earths with ammonia, or with primary potassium oxalate, or fractional decomposition of the nitrates by heat. Urbain (*Ann. Chim. Phys.*, [7], xix., 192), in 1900, denied the existence of philippia.

In this year of 1878, while studying the impure didymia from samarskite, Delafontaine (*Comptes Rendus*, lxxvii., 632) discovered a new oxide which he called decipia. Its metal had a high atomic weight ($R^{III}=159$), and it was characterised by the absorption bands λ 416 and λ 478. Lecoq de Boisbaudran (*Comptes Rendus*, lxxxviii., 322; lxxxix., 212) found, in a spectroscopic examination of a mixture of earths rich in didymia from samarskite, some new rays. In the spark spectrum there were four rays; in the absorption spectrum, two strong bands and three faint ones. The strong bands were in the blue, and had their centres at λ 480 and λ 4635. One of the other bands had a wave-length of λ 416, which had been ascribed by Delafontaine to one of the bands of decipia. Lecoq de Boisbaudran finally separated the earth giving these bands from didymia, and he called it samaria. Then Marignac (*Arch. des Sci. Phys. et Nat.*, [3], iii., 413), by fusion of the nitrates and fractionation of the double potassium sulphates, isolated two earths which he called Y_a and Y_b . The double potassium sulphate of Y_a was comparatively soluble in potassium sulphate solution; solutions of the earth gave no absorption spectrum, and the equivalent weight of the metal was about 120.5 (RO). Y_b , on the other hand, gave a double potassium sulphate less soluble in potassium sulphate solution; solutions of the earth gave an absorption spectrum corresponding to that of decipia, or better to that of samaria, and the metal had an equivalent weight of 115.6. Y_a has since been called gadolinium (*Comptes Rendus*, cii., 902). Delafontaine (*Comptes Rendus*, xciii., 63) again in 1881 showed that, by treating those earth sodium double sulphates most insoluble in a saturated solution of Glauber's salt with cold water, his decipia of two years before could be decomposed into two oxides, one with a metal equivalent of about 130 (RO) giving no absorption spectrum, the other with a base of much lower equivalent (not over 117) giving the absorption spectrum ascribed to the original decipia. He expressed the opinion that this second oxide and samaria were identical, as well as Marignac's Y_b . He also thought that the earth Y_a was a mixture of decipia and terbia, but Marignac pointed out that this could not be, because the oxide of Y_a was white, whereas that of terbiun was coloured. The oxide of Y_a and decipia were perhaps identical.

Cleve (*Comptes Rendus*, xcvi., 94; *Bull. Soc. Chim.*, [2], xliii., 162; *Chem. News*, liii., 30) has made an exhaustive study of samaria and its compounds. He isolated it by combining the methods of fractional precipitation with potassium sulphate solution, and with dilute ammonia. The atomic weight of samarium he found to be 150.02 (R^{III}). Its spark spectrum has been described by Thalén (*Sv. Vet. Akad. Handl.*, 1883, No. 7, p. 3; *Journ. de Phys.*, [2], ii., 446; *Ber. d. Chem. Ges.*, xvi., 2760), and by Lecoq de Boisbaudran (*Comptes Rendus*, cxiv., 575;

cxvi., 611, 674; cxvii., 199). The latter also studied its fluorescence spectrum. The body giving the spark spectrum he called Z_e , the one giving the fluorescence Z_f . Demarçay (*Comptes Rendus*, cii., 1551) found that samarium could be split into at least two simpler constituents. He used three methods, Welsbach's, fractional precipitation with ammonia, and another not given. He kept the name samarium for the element giving λ 407 and λ 400, and called the other provisionally S. Krüss and Nilson (*Ber. d. Chem. Ges.*, xx., 2134), in an article on the rare earths giving absorption spectra, also observed the fact that solutions containing samarium did not always give the same absorption spectrum. They obtained some solutions showing only λ 417, and the body to which this band was due they called S_{ma} . Crookes (*Proc. Roy. Soc.*, xl., 502) in 1886, following the fractionation of samarium by examination of the phosphorescence spectra, concluded that the samarium of gadolinite enclosed three components, while the samarium from samarskite contained a fourth. He also observed an anomalous ray in the phosphorescence spectrum of samarium (*Comptes Rendus*, cii., 1464). Its wavelength was 609, and the body to which it was due he called S_a . In 1891 Bettendorff (*Liebig's Ann. Chem.*, cclxiii., 164) obtained pure samaria by fractionation with ammonia, after the removal of ceria by fusion of the nitrates with potassium nitrate, the yttria group by treatment with potassium sulphate, and lanthana by decomposition of the nitrates by heat. He described the absorption spectrum, and denied that it had a phosphorescence one. He thought that samarium was a chemical individual. In 1893 Demarçay (*Comptes Rendus*, cxvii., 163) decided that, as far as the absorption spectrum showed, there was no reason to suspect the complexity of samarium. He examined four different fractions of Lecoq de Boisbaudran's samarium material. In 1900 Demarçay (*Comptes Rendus*, cxxx., 1185) separated samaria from neodidymia by fractional crystallisation of the magnesia double nitrates from nitric acid.

Crookes (*CHEM. NEWS*, liv., 39, 115) questioned the individuality of gadolinium, stating that its phosphorescence spectrum was practically identical with that of a mixture of 61 parts of yttria and 39 of samaria. Lecoq de Boisbaudran (*Comptes Rendus*, cviii., 165; cxi., 393) did not agree with him. Lecoq found, however, that Marignac's gadolinia contained about 10 per cent of impurities, and he succeeded in removing all but about 0.02 or 0.03 per cent of these. Crookes (*Comptes Rendus*, cii., 646) described its phosphorescence spectrum, and Lecoq (*Comptes Rendus*, cxi., 472) its spark spectrum. Bettendorff (*Liebig's Ann. Chim.*, cclxx., 376) separated gadolinia from samaria and terbina by fractionation with ammonia. He could get no spark spectrum, nor could Thalén. In 1896 Demarçay (*Comptes Rendus*, cxxii., 728) prepared gadolinia by fractional crystallisation of the earths rich in samaria from fuming nitric acid (sp. gr., 1.45), and gave the rays of its spark spectrum. Gadolinia was precipitated first, and samaria last. Between the two he discovered a new earth which he called Σ , characterised by its colourless salts with no absorption. The earth was colourless, which distinguished it from terbina; its spark spectrum was different from those of lanthana, ceria, gadolinia, ytterbia, terbina. It differed from gadolinia and samaria only in its spark spectrum. In 1899 Benedicks (*Zeit. Anorg. Chem.*, xxii., 393), using Marignac's method partly, and partly by fusion of the nitrates, then their fractionation from concentrated nitric acid, and lastly their precipitation by ammonia, prepared gadolinia and studied it. He could not obtain Demarçay's Σ . His gadolinia gave a spark spectrum, and the atomic weight of the metal was 156 (R^{III}). Demarçay (*Comptes Rendus*, cxxx., 1019), in 1900, was unable to isolate Σ , even after 800 fractions with the magnesia double nitrates; but since then he has isolated it sufficiently pure for characterisation (*Comptes Rendus*, cxxxii., 184). He has named it europium.

Marignac (*Arch. des Sci. Phys. et Nat.*, [2], liv., 97;

Comptes Rendus, lxxxvii., 578), in trying to isolate Delafontaine's philippia by partial decomposition of the nitrates by heat, discovered a new earth which he called ytterbia. It was colourless, and its metal had a high atomic weight ($R^{III} = 172.5$); further, it had no absorption spectrum. The method he used was a modification of Bahr and Bunsen's. He heated the nitrates till a portion was insoluble in hot water, whereas they heated only until the mass, which was entirely soluble in hot water, gave a crystalline precipitate of basic nitrates on cooling. In 1879 and 1880, Nilson (*Ber. d. Chem. Ges.*, xii., 550; xiii., 1430), using Marignac's method, isolated more ytterbia, and studied it. He found the atomic weight of the metal ytterbium to be 173. Pure ytterbia was obtained only after 400 or 500 ignitions. While working with this material, he obtained a white oxide whose metal equivalent was lower than that of ytterbia. This caused him to suspect the presence of another oxide, the metal of which had a lower atomic weight. By following the same method of fractionation, he succeeded in isolating this earth (*Ber. d. Chem. Ges.*, xii., 554; xiii., 1439). Its base had an atomic weight of 44, and proved to be identical with Mendeleeff's ekaboron, both in its properties and its atomic weight. He called his earth scandia. Cleve (*Bull. Soc. Chim.*, [2], xxxi., 486) also prepared scandia. His atomic weight of scandium was a unit higher than Nilson's, probably because of ytterbium in the material. The spark spectrum of ytterbia has been studied by Thalén (*CHEM. NEWS*, xlvii., 217; *Comptes Rendus*, xci., 326), and by Lecoq de Boisbaudran (*Comptes Rendus*, lxxxviii., 1342); and that of scandia by Thalén (*Comptes Rendus*, lxxxviii., 646; xci., 45; *CHEM. NEWS*, xlvii., 217).

(To be continued).

ANALYSIS OF THE VOLCANIC DUST FROM THE RECENT ERUPTION IN THE WEST INDIES.

WE are indebted to the kindness of Mr. B. E. R. Newlands for the following analysis of the volcanic dust which fell over the Barbados from La Soufrière, on May 8th, 1902:—

SiO ₂		51.60
Al ₂ O ₃		21.12
Fe ₂ O ₃		9.28
CaO		9.07
MgO		3.96
Na ₂ O		0.59
K ₂ O		0.81
SO ₃		Undetermined
P ₂ O ₅		do.

96.43

We hope next week to give the analyses of two similar dusts, one from Mont Pelée, which fell on the deck of the *Roddam*, and the other collected at Grenada.

Society of Public Analysts.—Testing for Arsenic.—The Secretary of the Royal Commission on Arsenical Poisoning having expressed the desire of the Commission to know to what extent the method of testing for and estimating minute traces of arsenic prescribed by the Joint Committee of the Society of Chemical Industry and of the Society of Public Analysts has been adopted, and with what results, the Secretaries of the above Society have issued a slip containing four questions which they request may be replied to as concisely and briefly as possible and returned to them. The questions are:—1. Have you used the method; and if so, to what extent? 2. Have you found it advantageous, and do you consider it preferable to other methods? 3. Have you met with any, and if so what, difficulties? 4. Have you any suggestions to offer with regard to the better working of the method?

THE ESTIMATION OF DISSOLVED OXYGEN IN WATER.

By WILLIAM NAYLOR, F.C.S., A.M.I.C.E.

THE estimation of dissolved oxygen in river water and sewage works effluents has now become quite common, and the following method, devised by B. W. Gerland, as practised by the author, may be of interest. Though not applicable for river-side estimations, nor sufficiently "handy" for single estimations, it has been found very serviceable for the work of a station where a great number of samples, say 40 or 50, have to be examined in one day.

Its principle, as described by Dr. Gerland (*Journ. Soc. Chem. Ind.*, xv., p. 15; xviii., p. 340) is the reduction of indigo by sodium hyposulphite, and this is now brought into daily

the burette, c, which burette is charged from time to time by means of the tube b, having clip at q. With the indigo reduced in the Woulff's bottle, the liquid will remain a pale straw-colour if the atmosphere is oxygen free, and as soon as this is the case the hypo is standardised against the indigo solution.

After standardising, the contents of the bottle are at neutral tint, and about 100 c.c. of the sample under examination are passed in by means of the thistle funnel, m, provided with tap, and the quantity of hypo required noted, as a guide. It is important that the funnel dip right into the liquid to prevent any yield of oxygen to the atmosphere of coal-gas.

With the contents at neutral tint after discovering the hypo required for 100 c.c. of sample, a little under two and a-half times this amount of hypo is now run into the bottle, and then 250 c.c. of the sample. A faint blue colour is produced, and this is removed by the addition of a drop or two of hypo and the total for the 250 c.c. of sample entered.

Any number of samples can be done in succession, the bottle being drawn off as necessary by means of the tube o and clip t.

The following are two note-book entries, the first of which was found to be in agreement with standard aerated water as per table of Roscoe and Lunt, and also with a eudiometric estimation after boiling from a completely filled flask and running in warm mercury is:—

10 c.c. indigo solution (neutralised with sodium bicarb. before use) required 24.5 c.c. hypo.

Indigo sol. contained 8.321 grms. indigo-tine per litre.

1 c.c. indigo sol. contained available oxygen 0.0005.

24.5 c.c. hypo = 0.005 oxygen.

250 c.c. sample of aerated water required 12.5 c.c. hypo = 0.0025 grm. oxygen.

1000 c.c. = 0.01 grm. oxygen.

$$\frac{0.01 \times 1000}{1.4336} = 7.0 \text{ c.c. oxygen per litre.}$$

Bacterial Filter Effluent, after shaking to saturation.

10 c.c. indigo sol. required 37.0 c.c. hypo.

250 c.c. sample required 10.0 c.c. hypo = 0.00135 grm. oxygen.

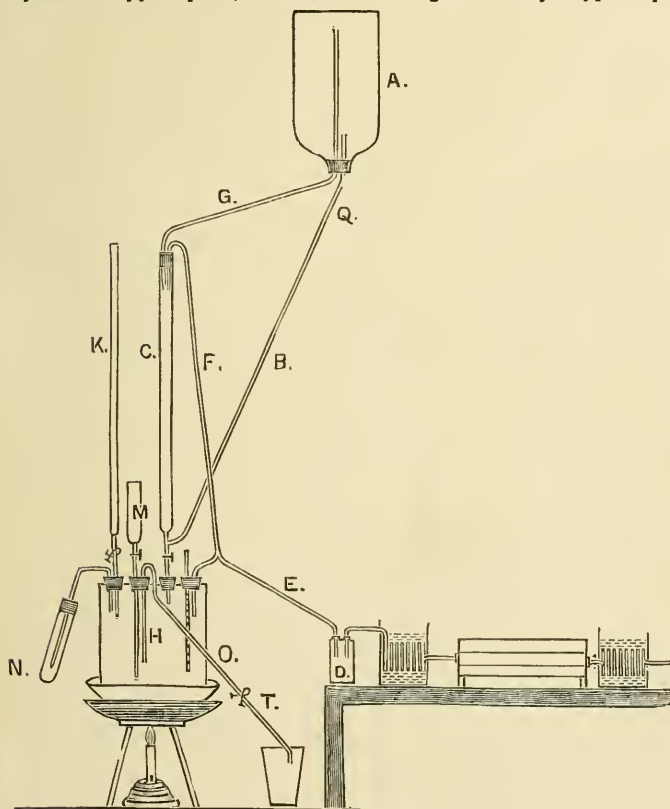
1000 c.c. sample = 0.0054 grm. oxygen.

$$\frac{0.0054 \times 1000}{1.4336} = 3.77 \text{ c.c. oxygen per litre.}$$

The method is not nearly so complicated or cumbersome as it appears at first glance, and the apparatus once set up will give very little trouble. In an investigation just completed, on "The Movement of the Polluted Zone in the Ribble Estuary," it was found that a hundred samples could be examined in one day, without any necessity for washing out the Woulff's bottle.

Ribble Joint Committee's Laboratory,
Preston, May 20, 1902.

Estimation of Starch in the Grains of Cereals.—M. Lindet.—This method is based on the attack of the grains by means of hydrochloric pepsine, which dissolves the gluten, on the kneading of the mass in a silk bag, and on the collection of the starch. The author has modified the latter part of the estimation, and replaced it by decantation and saccharification, after which the glucose and dextrine formed are weighed.—*Bull. Soc. Chim. de Paris*, xxv., No. 24.



quantitative use owing to the accessibility of pure indigo, and the tedious process of standardising against aerated water avoided.

The pure indigo, obtainable from the Badische Aniline and Soda Works, Ludwigshafen, after washing with water and hydrochloric acid and alcohol, and treating with a solution of persulphate of ammonia in acid solution, will be found, after reduction, to require the theoretical amount of oxygen for oxidation.

In examining a sample of water, the four-necked Woulff's bottle, H, is first charged with a small quantity, about 50 to 100 c.c., of tap water by means of the thistle funnel, M, and a stream of coal-gas which has been passed through a heated copper tube, filled with copper turnings, is sent also into the bottle via the tube E and out by water seal, N.

A branch, F, from the tube E conveys some of this de-oxidised coal-gas to top of hypo reservoir, A, and burette c. Into the water in the bottle are now run one or two c.c. of indigo solution, and these are reduced exactly by hypo from

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, May 15th, 1902.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. James Handby Ball, St. Stephen's Villa, Limerick; Bryce Chudleigh Burt, University Settlement, Bermondsey, S.E.; Arthur Crozier Claudet, 27, Daleham Gardens, Hampstead, N.W.; Edgar William Foll, 40, Sutton Street, Lambeth, S.E.; John Longsdon Garle, 136, Holland Road, Kensington, W.; Geo. H. Leader, Sexey's School, Blackford, Somerset; James Butler Moody, 111, Manchester Road, Burnley, Lancs.; Percy Philip Phillips, Haslemere, Morris Avenue, Manor Park, E.; William E. F. Powney, 67, Barretts Grove, Stoke Newington, N.; William C. S. Stanger, 72, Belle Vue Road, Ipswich.

Of the following papers, those marked * were read:—

*74. "*The Variation with Temperature of the Surface-tensions and Densities of Liquid Oxygen, Nitrogen, Argon, and Carbon Monoxide.*" By E. C. C. BALY and F. G. DONNAN.

The measurements were made by the method of elevation in capillary tubes. The surface tensions, molecular surface-energies, and densities of liquid oxygen, nitrogen, argon, and carbon monoxide have been determined between the temperatures of 70° and 90° (absolute). In the case of argon, owing to the proximity of its freezing- and boiling-points, measurements could only be made between 84° and 89°.

The relation between molecular surface energy and temperature is found to be linear, thus agreeing with the results obtained by Eötvös and by Ramsay and Shields for non-associated liquids.

The values found for $\frac{d}{dt} \gamma (Mv)^{\frac{2}{3}}$, the temperature coefficient of the molecular-surface energy, are as follows:—

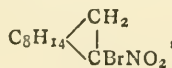
Oxygen	1'917
Nitrogen	2'002
Argon	2'020
Carbon monoxide . . .	1'996

The average value obtained by Ramsay and Shields for non-associated liquids was 2'212.

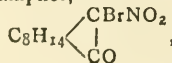
Continuations of the straight lines connecting molecular surface energy and temperature so as to cut the temperature axis give values for the temperature which in the case of oxygen and nitrogen agree very closely with the critical temperatures as determined by Olszewski. In the case of argon and carbon monoxide, the temperatures so found do not agree with the critical temperatures as previously determined.

*75. "*Comparison of Bromonitrocamphane with Bromonitrocamphor.*" By M. O. FORSTER.

The close relationship between 1:1-bromonitrocamphane,—



and $\alpha\alpha$ -bromonitrocamphor,—



led to the expectation that the series of changes by which the former substance is converted into a hydroxylic isomeride of camphor might be applied to bromonitrocamphor, and thus give rise to a hydroxylic isomeride of camphorquinone. Bromonitrocamphor was therefore heated with alcoholic silver nitrate until silver bromide was no longer precipitated. This treatment, which transforms

bromonitrocamphane into nitrocamphene, $\text{C}_{10}\text{H}_{15}\text{NO}_2$, proceeds very slowly in the case of the camphor derivative, the solution becoming yellow. Instead of the expected nitro-compound, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{NO}_2$, the only crystalline product obtained was camphorquinone. The yield of quinone by the new method amounted to 25 per cent; the process therefore compares favourably with that of Claisen, but is more tedious.

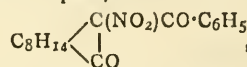
The comparison of bromonitrocamphane with bromonitrocamphor has been extended to the behaviour of these substances towards phenylhydrazine. The uncontrolled action of the base is exceedingly vigorous and yields no definite product; under regulated conditions, however, bromonitrocamphane is reduced to nitrocamphane, which may be thus obtained in a purer form than has been possible hitherto. Nitrocamphane prepared by this method melts at 157° instead of 147–148°, and has $[\alpha]_D = +27\cdot0^\circ$ in benzene, and $+7\cdot4^\circ$ in absolute alcohol, instead of $20\cdot4^\circ$ and $4\cdot6^\circ$ respectively.

In the case of bromonitrocamphor, phenylhydrazine gives rise to nitrocamphor in a form which requires to be crystallised only once from petroleum to produce the substance in the colourless state, melting at 103° and giving $[\alpha]_D = -123\cdot8^\circ$ in benzene; as the yield amounts to 84 per cent of the theoretical, this method appears to be a distinct improvement on the existing process.

Bromine has no action on bromonitrocamphor under conditions which lead, in the case of bromonitrocamphane, to elimination of the nitro-group and production of a tribromo-derivative. Bromonitrocamphor is also indifferent towards nitric acid, which transforms bromonitrocamphane into a new lactone; alkalis eliminate hydrogen bromide from this compound, yielding salts of an unsaturated acid containing nitrogen. These derivatives are being investigated.

*76. " *$\alpha\alpha$ -Benzoylnitrocamphor and $\alpha\alpha$ -Benzoylodocamphor.*" By M. O. FORSTER and E. A. JENKINSON.

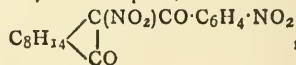
$\alpha\alpha$ -Benzoylnitrocamphor,—



prepared by heating 5 grms. of enolic benzoylcamphor dissolved in 25 c.c. of glacial acetic acid with 1·5 c.c. of fuming nitric acid, is also produced when nitrogen peroxide is passed into a solution of benzoylcamphor in dried chloroform. It requires 40 parts of boiling alcohol to dissolve it and is sparingly soluble in common solvents, crystallising in rectangular plates which melt and evolve gas at 225°. A 2 per cent solution in chloroform has $[\alpha]_D = +245\cdot2^\circ$. It is insoluble in aqueous alkalis, is indifferent towards ferric chloride, and does not give Liebermann's reaction.

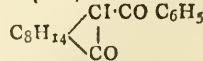
Attempts to convert the substance into $\alpha\alpha$ -benzoylaminocamphor and $\alpha\alpha$ -benzoylhydroxylaminocamphor have been unsuccessful, but it is readily hydrolysed by alcoholic potash, yielding α -nitrocamphor and benzoic acid.

$\alpha\alpha$ -Nitrobenzoylnitrocamphor,—



produced when benzoylnitrocamphor is dissolved in fuming nitric acid, is more readily soluble than the foregoing substance, and crystallises from alcohol in pale yellow leaflets which melt and evolve gas at 176–177°; a 2 per cent solution in chloroform has $[\alpha]_D = +190\cdot6^\circ$. Hydrolysis with alcoholic potash resolves the substance into nitrocamphor and m -nitrobenzoic acid.

$\alpha\alpha$ -Benzoylodocamphor,—



is not obtainable by the methods which give rise to the benzoylbromocamphors and benzoylchlorocamphors; it is

prepared by adding a solution of iodine in potassium iodide to enolic benzoylcamphor dissolved in aqueous potash. The compound crystallises from alcohol in pale yellow plates which become reddish brown when exposed to light; it melts at 136° . A 2 per cent solution in chloroform has $[\alpha]_D = +47.7^{\circ}$.

Benzoyliodocamphor is not converted into an isomeride by the action of hydrobromic acid, and hydriodic acid merely reduces it. Solutions in organic liquids rapidly undergo decomposition, with liberation of iodine; ferric chloride soon produces a pale green colour, becoming bluish, and finally purple. Attempts to convert the substance into benzoylcyanocamphor and benzoylhydroxycamphor have been unsuccessful.

*77. "2:4-Dibromo-5-nitro- and 2:4-Dibromo-3:5-dinitro-toluenes and their Behaviour on Reduction." By W. A. DAVIS.

On nitration with fuming nitric acid, 2:4-dibromotoluene gives 2:4-dibromo 5-nitrotoluene, which is converted by reduction with tin and hydrochloric acid into 4:6-dibromo *m*-toluidine, the acetyl-derivative of which crystallises from alcohol in small white prisms (m. p. 167°).

If the nitration of 2:4-dibromotoluene be not carefully regulated, 2:4-dibromo-3:5-dinitrotoluene is obtained. It crystallises from ethyl acetate in yellow prisms (m. p. 127.5°), and differs from all the other bromo- and dibromonitrotoluenes, as it loses the whole of its bromine on reduction with tin and hydrochloric acid, giving *s*-toluenediamine; the diacetyl-derivative, $C_6H_3Me(NHAc)_2$, crystallises from alcohol in small hemimorphic prisms (m. p. $236-237^{\circ}$) and is strongly electric. The removal of the bromine atoms from 2:4-dibromo-3:5-dinitrotoluene during reduction is apparently due to the influence of the two contiguous nitro-groups.

*78. "Note on the Purification of Hydrochloric Acid from Arsenic." By L. T. THORNE, Ph.D., and E. H. JEFFERS.

In the estimation of arsenic by the Marsh-Berzelius test, the use of hydrochloric acid is admittedly preferable to that of sulphuric acid. It is, however, practically impossible to purchase hydrochloric acid really free from arsenic, and it is therefore necessary to remove the last traces of arsenic from it in the laboratory.

The method recommended in the report of the Joint Committee of the Society of Chemical Industry and of Public Analysts (*Analyst*, 1902, xxvii., 48), namely, that of treatment of the diluted acid with hydrobromic acid or bromine and sulphurous acid and subsequent distillation, is successful in most cases, but occasionally fails; the arsenic then appearing to be present in a very stable or resistant form. Under these latter conditions, satisfactory results are said to be obtained if the hydrobromic and sulphurous acids are added to the strong hydrochloric acid, and the excess of hydrochloric acid gas boiled off before distillation commences. If large quantities of hydrochloric acid are wanted, this method is inconvenient and wasteful, owing to the large quantities of hydrochloric acid gas evolved.

The whole of the arsenic may readily be removed by means of a modification of the well-known Reinsch test for arsenic in the following manner:—

The hydrochloric acid to be purified is diluted with water till its specific gravity is about 1.10, then raised to the boiling-point, and a piece of fine copper gauze introduced. The gauze should be of about 10 meshes to the inch, and of as pure copper as possible. When a couple of litres of liquid are being dealt with, the gauze should be about four inches square and coiled very loosely (about $1\frac{1}{2}$ to 2 turns) round a long glass rod flattened at the end, as in this way it can be readily introduced and removed, besides being brought into better contact with the liquid. The whole is then kept just boiling for an hour. By this time the gauze will have become more or less blackened, and should be replaced by a second piece and the diges-

tion continued for another hour. If this piece is also blackened, a third is used, and so on, until the gauze remains perfectly bright after about an hour's digestion. With moderately good acid, two, or at most three, pieces of gauze are sufficient. The gauze is then removed, and the acid at once transferred to a retort and distilled from a fresh piece of gauze. It is advisable, as a precaution, to reject the first 20 per cent of the distillate, though even this is very rarely contaminated if the digestion is carefully carried out, and from 100 to 200 c.c. should be left behind in the retort. The method is simple and requires but little attention, and it is not necessary to use the purest acid; even good muriatic acid, "commercially free from arsenic," may be satisfactorily employed. The acid obtained is the constant boiling-point acid, which is about the most suitable strength for use in the Marsh-Berzelius test.

The gauze must, of course, be gently ignited before being used, and should not be introduced until the acid is just beginning to boil. It is also preferable not to allow the digested liquid to cool in contact with the air before transferring to the retort, as the copper gauze would be much attacked and its efficiency for the present purpose considerably lessened by the consequent oxidation.

79. "The Radio-activity of Thorium Compounds. Part II. The Cause and Nature of Radio-activity." By E. RUTHERFORD and F. SODDY.

The authors find that thorium from which ThX has been separated regains its activity with time, whilst the activity of ThX decreases with time. At the end of three weeks, the activity of the former again reached a maximum value, and the activity of the latter almost completely disappeared.

ThX possesses a distinct chemical behaviour which differentiates it from thorium. Ammonia is the only reagent of those tried capable of separating it from the latter. Ammonium carbonate, oxalic acid, and sodium phosphate give precipitates with normal activity, and the residues from the filtrates are inactive.

Using the radio-activity of the residues from the filtrates after precipitation of the thorium by ammonia, as a means of determining the amounts of ThX present, it was found that the amounts produced in varying intervals of time between successive precipitations agree with the requirement that ThX is being continuously produced by thorium compounds at a constant rate.

The rate of production of ThX and the rate of decay of its activity are apparently unaffected by known agencies. Both changes proceed independently of the chemical and physical conditions of the molecule.

The source of the energy required to maintain the radio-activity of thorium over indefinite periods is therefore to be found in a chemical change producing new types of matter.

Many of the results obtained by the authors in their investigation of the thorium emanations are now capable of explanation. Emanating power appears as a property of ThX and not of thorium, and is proportional to the activity of the ThX present. The decay and recovery of emanating power of ThX and thorium are completely analogous to the decay and recovery of radio-activity. These results find their simplest explanation in the view that a secondary change is proceeding in ThX. One of the products is gaseous, and in the radio-active state constitutes the emanation. This change appears more allied to ordinary chemical reaction than the primary, for it is affected by the conditions.

The residual activity of thorium would be explained if the chemical change which produces ThX produces also a second kind of active matter, closely allied to thorium in its properties. The radiations of this residual part are composed entirely of rays non-deviable in the magnetic field, whereas the other two components of thorium radio-activity comprise both deviable and non-deviable radiation. In this respect uranium and thorium are analogous (compare following paper).

The present result, that radio-activity is the consequence of changes— independent of the conditions—in which new types of matter are formed, leads to the conclusion that radio-activity is the manifestation of sub-atomic chemical change.

80. "The Radio-activity of Uranium." By F. SODDY.

During an investigation of the radio-activity of uranium (conjointly with Prof. Rutherford) great differences arose between the results obtained and those of previous workers. These are traced to the methods employed for measuring radio-activity.

UrX prepared by Crookes's original method (*Proc. Roy. Soc.*, 1900, lxvi., 409), although intensely active to the photographic plate, is almost inactive to the electrometer under ordinary circumstances. The uranium from which it is separated is inactive to the sensitive film, but its activity to the electrometer is very nearly normal.

This is due to the dual character of uranium radiation (Rutherford, *Phil. Mag.*, 1899, [5], xlvii., 109). The α - or easily absorbed radiation is without appreciable action on the photographic film, and contributes by far the major portion of the ionisation effect observed by the electrometer. The β - or penetrating radiation, on the other hand, causes the whole of the photographic effect, but being little absorbed by gases, and constituting but a small proportion of the total radiation, its ionisation effect cannot be well observed by the electrometer without special arrangements.

UrX possesses all the β - with none of the α -radiation, the latter being completely retained by the uranium. The β - is wholly deviable in the magnetic field, the α -radiation not at all. This explains the conclusion of Becquerel (*Comptes Rendus*, 1902, cxxxiv., 208), who worked solely with the photographic method, that the whole of the uranium radiation is deviable in the magnetic field.

The discovery of Becquerel that inactive uranium recovers its activity with time (*Comptes Rendus*, 1901, cxxxiii., 977) therefore points to a continuous production of UrX by the uranium. This continuous production can be observed by means of the β -radiation in uranium originally freed from UrX a'ter three days.

The published methods of Crookes (*loc. cit.*) and Becquerel (*Comptes Rendus*, 1900, cxxxi., 137) fail to remove the α -radiation of uranium, or even to diminish its quantity. As in the case of thorium, this constitutes a residual activity comprising only non-deviable radiation, and it has not yet been found possible to remove it by chemical means. Experiment shows that if it is a secondary radiation caused by UrX, it must take over a year to decay to half its value after the exciting cause is removed. It seems therefore more probable that it is caused by a second type of non-uranium matter, produced from the uranium by the same change as the UrX.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before June 9th.

NOTICES OF BOOKS.

A Bibliography of the Analytical Chemistry of Manganese, 1785-1900. By HENRY P. TALBOT and JOHN W. BROWN. Smithsonian Miscellaneous Collections, 1313. City of Washington, 1902. 8vo. viii.-124 pp.

THIS forms one of the series of Indexes to Chemical Literature prepared under the auspices of the Committee of the American Association for the Advancement of Science, and recommended by them to the Smithsonian Institution for publication. The compilers in their preface acknowledge their indebtedness to a similar work by H. Carrington Bolton published twenty-five years ago, and to

Brearley's "Bibliography of Steel Works Analysis" in the CHEMICAL NEWS. The periodicals examined number fifty-four, comprising several hundred volumes. The references are arranged chronologically, and are followed by a full subject-index and an author-index, the two occupying 27 pages, double columns. The work will prove of value to analytical chemists, especially to those desirous of becoming acquainted with the results of the labours of their predecessors. Students of the history of analytical methods will also find this invaluable. Its handsome paper and typography does credit to the Smithsonian Institution and to the printers.

Index to the Literature of the Spectroscope (1887-1900, both inclusive). Continuation of the previous Index, by the same Author, published in 1888. By ALFRED TUCKERMAN. Smithsonian Miscellaneous Collections, 1312. City of Washington, 1902. 8vo. iii.-373 pp.

THIS second volume of Dr. Tuckerman's well-known bibliography brings the literature down to the end of the nineteenth century, after which date the International Committee for Indexing Scientific Literature will continue the work.

The arrangement is satisfactory: first, the reference to literature is placed under the author's name, the latter in alphabetic order; and, secondly, a classified subject-index, in which the references are briefly repeated. Of course, it is often difficult to select topics that should be included or excluded, and we notice a few that seem to be out of place; on the whole, it is better to err by including foreign matter than by excluding the pertinent factors.

The thanks of all physicists and chemists are due to Dr. Tuckerman for continuing this arduous labour of love—for such it has been—and to the Smithsonian Institution for the handsome dress in which it appears.

Indicators and Test-papers; their Source, Preparation, Application, and Tests for Sensitiveness. A résumé of the Current Facts regarding the Action and Application of the Indicators and Test-papers which have been proposed from time to time, and are in present use in Chemical Manipulations. With a Tabular Summary of the Application of Indicators. Designed for the Use of Chemists, Pharmacists, and Students, by ALFRED I. COHN. Second Edition, Revised and Enlarged. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1902. 12mo. Pp. ix.-267.

THE first edition of this useful little book was noticed in the CHEMICAL NEWS for November 3, 1899 (vol. lxxx., p. 219). Since then some errors have been corrected, and the entire work has been brought down to date by the addition of an appendix embodying the information on the indicators introduced in the intervening years. Perezol is one of the new indicators (of Mexican origin) perfectly adapted for titrating alkalis, reacting with great delicacy; it is particularly useful in estimating the alkalinity of potable waters, &c.

In each section, Indicators and Test-papers, an alphabetic arrangement is adopted, making it easy to refer to a given topic. There is an uncommonly full index.

H. C. B.

Class List and Index of the Periodical Publications in the Patent Office Library. London: Darling and Son, Ltd., and The Patent Office. 1902. Pp. 91.

THE heading "Periodical Publications" includes Journals, Transactions of Societies, Year-books, Reports of Congresses, Departments, &c.

This handbook is divided into three sections—(a) An abstract of the classifications adopted; (b) a classified catalogue; (c) a brief alphabetical title index.

The collection is divided into ten primary classes, lettered A to K (omitting I), each of which is divided into sub-classes, numbered consecutively, and in some cases the sub-classes are further subdivided according to locality. Following the class-mark is the size-mark, which is indicated thus:—Colon (:) for works under 13 inches; slant rule (/) for works between 13 and 17 inches; parallel mark (||) for works over 17 inches wide. After the size-mark comes the work-mark; that is, the mark used to distinguish a given work from its fellows in a class.

The present list comprises 2563 works, distributed under 356 classes, and representing some 39,682 volumes.

Atoms and Energies. By D. A. MURRAY, A.M., sometime Instructor in the Government Shogyo Gakko Kyoto, Japan. London: Gay and Bird. 1901.

STARTING with the assumption that the chemical atoms are all identical in substance, and accepting only two energies—one attraction or gravitation, and the other repulsion—the author considers in succession Chemical Affinity, Cohesion, Adhesion, Latent Heat, Magnetism, and Electricity, and attempts to give a rational explanation for these phenomena. His fundamental point is to regard the atoms of matter, not in the usual conception of small spherical particles, but as of very diverse shapes and sizes, and then with the two energies, gravitation and repulsion, to suggest that "all the so-called chemical potencies or attributes residing in the atoms, which differentiate them one from another, are simply the result of differences of shape."

The author shows ingenuity in his arguments; and what makes the book readable is the entire absence of that dogmatism so general in works of this kind; the ideas are merely put out as suggestions to "stimulate thought."

The final conclusion is, that "energy is a distinct entity," not a mode of motion; or, in other words, energy is that mysterious something which we have had to call Ether.

In an introductory chapter, Prof. Frederick Starr, of Chicago, speaks very highly of the work, considering the author's "point of view novel, the argument clear, and the book itself satisfactory."

It would scarcely be fair to the author in a notice of this kind to comment on any particular passage or point raised; the book must be studied as a whole, and the originality of the ideas certainly has the effect of stimulating thought and helps to guard one against the unfortunate habit of what Prof. Starr terms "giving some grand name to a difficult phenomenon and feeling about as well satisfied as if we had explained it."

CORRESPONDENCE.

ERRORS IN CHEMICAL TEXT-BOOKS.

To the Editor of the Chemical News.

SIR,—In Smith's translation of "Richter's Organic Chemistry" (vol. i., p. 240), I notice a very curious error in the description of some of my own work.

The reaction between sodium-ethyl and carbonic acid is properly set forth by the well-known equation, but there is the amusing statement, "This reaction is only applicable with sodium-methide and sodium-ethide."

In the *Fahresbericht* for the year 1868 (p. 523) there is an account of the preparation of caproate of soda by the action of sodium-amyl upon carbonic acid, and there can be no doubt whatever that the reaction is general and of the widest scope.

The action of sodium upon the compounds of zinc with the alcohol radicals takes place with great readiness, and

the action of carbonic acid upon the resulting sodium compound is one of the quickest known to chemists. It is in the highest degree improbable that any term of the series of zinc organo-metallic compounds would fail to yield the corresponding sodium derivative, or that the sodium derivative would fail to react with carbonic acid.—I am, &c.,

J. ALFRED WANKLYN.

The Laboratory, New Malden,
May 26, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiv., No. 18, May 5, 1902.

Glucose and Carbonates of Cerium. A New Method of Oxidation.—André Job.—The author examined the mechanism of the spontaneous oxidation of cerous carbonate dissolved in an alkaline liquor producing active oxygen. The carbonate of the peroxide which is formed from this in the cold by simple contact with air is an oxidising agent which allows of the formation of hydrogen peroxide when it is dissolved in acids. Recently M. Baur developed an application of these properties. By agitating with air an alkaline solution of cerous carbonate added to potassium arsenite, the oxidation of the latter is effected, and this fact verifies the assumption that the total quantity of oxygen fixed corresponds to the primary formation of the peroxide. The author continues these researches, and describes various experiments on the effect of glucose in causing the peroxidation of the cerium salt.

Alloys of Cadmium with Barium and Calcium.—Henri Gautier.—The author examines the conditions of formation and decomposition of the hydrides of the alkaline earths. It is not possible to produce these hydrides directly from the free metal, because, with the exception of calcium, they are not known in a state of purity. He therefore uses the alloys of the metals with an easily volatile metal, such as mercury or cadmium. The alloys of the alkaline earth metals with cadmium being easier to obtain pure and more concentrated than the corresponding amalgams, they are used by preference. He describes the preparation of the barium and calcium alloys, that of strontium having been already described.

An Oxy-carbide of Cerium.—Jean Sterba.—The author obtains a well-defined and perfectly crystalline oxy-carbide of cerium having a formula $CeC_2 \cdot 2CeO_2$, which is always formed at the beginning of the reduction of the oxide by carbon. This oxy-carbide is relatively stable in water and air. During its decomposition by acids it yields non-saturated hydrogen carbides. No other carbide except CeC_2 is formed in the electric furnace and an oxy-carbide of formula $CeC_2 \cdot 2CeO_2$.

Arsenic Anhydride and its Hydrates.—V. Auger.—The author performs a number of experiments on the effect of heat on $(AsO_4H_3)_2H_2O$. He finds that the only hydrates possible to obtain are $(AsO_4H_3)_2H_2O$ and $As_2O_3 \cdot H_6O$. The hydrates AsO_4H_3 , $As_2O_7 \cdot H_4$, and AsO_3H , described by Kopp, have not been obtained. Arsenic anhydride is produced at about 180° ; it is stable even at 490° , but decomposes at a dull red heat, and cannot be obtained in a molten state.

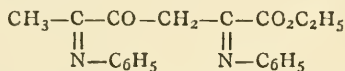
Preparation and Properties of Chloro-, Bromo-, and Iodo-sulphobismuthates of Lead.—Fernand Ducalte. Sommerlad prepared certain sulphoarsenites and sulphoantimonites existing in nature by allowing a metallic chloride to act on arsenic or antimony sulphides. Col-

sidering the chemical analogy of arsenic and antimony with bismuth, the author applies the same reaction to produce natural mineral sulphides of the latter metal. His researches as to the time of heating the mixture employed and the temperature to which it should be heated show that it is impossible to eliminate chlorine, but he succeeds in obtaining perfectly crystalline compounds of sulphobismuthates with chloro-, bromo-, and iodo-sulphides of bismuth. He therefore concludes that the presence of the halogen element in the products obtained by the action of lead chloride, bromide, or iodide on bismuth sulphide is not exceptional, and the proportion of the halogen element is determined by the general formula $PbS, Bi_2S_3, 2BiSX$, in which X can represent Cl, Br, or I.

Certain Derivatives of Pyruvyl-pyruvic Ether.—L. J. S. mon.—In spite of the interest which attaches to its discovery very little is known of pyruvyl-pyruvic ether—



During the action of aniline on ethyl-pyruvate the author isolates a compound—



By replacing the ethyl-pyruvate with another pyruvic ether and using paratoluidine in place of aniline, he obtains a series of compounds analogous to the preceding, and from a comparison of these he proposes the above formula.

Mutual Action of Acid Chlorides and Methanal.—Marcel Descudé.—The action of an acid chloride on methanal may be expressed by the three following equations:—

- $C_6H_5-COCl + CH_2O = C_6H_5-COOCH_2Cl.$
- $\left\{ \begin{array}{l} C_6H_5-COOCH_2Cl \\ C_6H_5-COOCH_2Cl \end{array} \right. = \left\{ \begin{array}{l} C_6H_5-CO \\ C_6H_5-CO \end{array} \right\} O + O < \left\{ \begin{array}{l} CH_2Cl \\ CH_2Cl \end{array} \right.$
- $\left\{ \begin{array}{l} C_6H_5-CO \\ C_6H_5-CO \end{array} \right\} O + CH_2O = \left\{ \begin{array}{l} C_6H_5-COO \\ C_6H_5-COO \end{array} \right\} CH_2.$

Compounds of Tetrazoditolylsulphite of Sodium with the Aromatic Amines and the Phenols, and their Transformation into Azoic Colouring-matters. —M.M. A. Seyewetz and Biot.—The authors find that the aromatic amines give with sodium tetrazoditolylsulphite compounds which can be transformed into azoic colouring matters by the action of light or by prolonged boiling with alcohol. They examine the theory of this transformation.

Addition of Hypochlorous Acid to Propylene.—Louis Henry.—This paper is an answer to Marc Tiffeneau's remark in a paper in the *Comptes Rendus* of April 7, 1902, on the subject of "The Constitution of the Chlorhydrines," in which he states that, contrary to Henry's assertion, during the fixation of ClOH on to propylene the oxyhydride gives up to the carbon the least quantity of hydrogen, giving the chlorohydrine, $CH_3-CHOH-CH_2Cl$. The author now endeavours to re-establish his own statement.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxv., No. 23.

Qualitative and Quantitative Estimation of Traces of Antimony in the presence of Large Quantities of Arsenic.—G. Denigès.—Already inserted.

Estimation of the Phosphoric Acid in Phosphates.—J. A. Muller.—Already inserted.

Estimation of Tin by Lenssen's Method.—J. A. Muller.—Already inserted.

Analysis of Tin Ores.—J. A. Muller.—Already inserted.

MEETINGS FOR THE WEEK.

MONDAY, June 2nd.—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "A Contribution to the Chemistry of Whiskey," by Dr. Philip Schridrowitz, F.C.S. "The Estimation of Perchlorate in Saltpetre, &c.," by Dr. A. Dupré, M.A., F.R.S. "On the Will Test for Nitrocellulose," by Dr. Robert Robertson, M.A. "On the Effect of the Alcohol Duty on Chemical Industries," by Dr. O. Silberrad.

TUESDAY, 3rd.—Royal Institution, 3. "The Laws of Heredity, with special reference to Man," by Prof. Carl Pearson, M.A., F.R.S.

THURSDAY, 5th.—Royal Institution, 3. "Contemporary British Sculpture," by M. H. Spielmann. Chemical, 8. "The Action of Ungerminated Barley Diastase on Starch" (Part I.), by J. L. Baker. "The Decomposition of Chlorates—Part V., Potassium Chlorate in presence of Oxides of Manganese," by W. H. Sodeau.

FRIDAY, 6th.—Royal Institution, 9. "The Nile Reservoir and Dams," by Sir Benjamin Baker, K.C.M.G., LL.D., D.Sc., F.R.S., M.Inst.C.E.

SATURDAY, 7th.—Royal Institution, 3. "The Development of the English Drama—III., The Drama under Elizabeth," by Prof. Brander Matthews, Litt.D., D.C.L.

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THE CHEMICAL NEWS.

VOL. LXXXV., No. 2219.

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS OF THE YTTRIUM GROUP.*

I.

By L. M. DENNIS and BENTON DALES.

(Continued from p. 253).

Historical (continued).

SORET (*Comptes Rendus*, lxxxvi., 1062), by a spectroscopic examination of Marignac's erbia and terbia materials, found a series of absorption bands which did not belong to erbia or to any other of the known elements. He called the earth giving them X. Cleve (*Comptes Rendus*, lxxxix., 478), in 1897, showed that by fractional decomposition of the nitrates by heat, erbia free from ytterbia and scandia could be separated into three earths, each characterised by an absorption spectrum which was a portion of the one ascribed to old erbia. The metals in these earths were the true erbium, with an atomic weight of about 166 (*Comptes Rendus*, xci., 381); holmium, and thulium with an atomic weight of about 170.7 (*Comptes Rendus*, xci., 328). Soret (*Comptes Rendus*, lxxxix., 521) stated that holmia and his earth X were identical, and Cleve (*Comptes Rendus*, lxxxix., 708) admitted this to be true. Delafontaine maintained that his philippia was identical with both of these, but Cleve could not establish this fact. Delafontaine himself afterwards admitted that his philippia had no absorption spectrum. Lecoq de Boisbaudran (*Comptes Rendus*, cii., 1003, 1005) proved, by making many hundreds of fractions with ammonia and with potassium sulphate and alcohol, that the holmia spectrum could be divided into two portions, the bands characteristic of one being λ 640.4 and λ 536.3, and of the other λ 451.5 and λ 753. Since the first two bands were the ones by which Cleve and Soret originally characterised the element holmium, he kept this name for the one giving them; the one to which the other bands were due he called dysprosium. Crookes (*Proc. Roy. Soc.*, xl., 502) soon after Lecoq's announcement, stated that he had isolated an earth in this group giving only the absorption band λ 451, and that therefore dysprosium was probably still a complex substance. Lecoq has expressed the same opinion. Krüss and Nilson (*Ber. d. Chem. Ges.*, xx., 2134) showed, by a spectroscopic examination of the absorption bands of the rare earths obtained from many different minerals, that the variations in intensities of the bands as found in these minerals, could be accounted for only upon the assumption that the bands belonged to different individuals. As a result of this, they considered what we now call erbia to be made up of two components, thulia of two, holmia of four, and dysprosia of three. Hofmann and Krüss (*Zeit. Anorg. Chem.*, iii., 407) in 1893 concluded, as a result of their aniline hydrochloride fractionation, that holmium was a complex substance; Krüss (*Zeit. Anorg. Chem.*, iii., 353) alone has thrown doubt upon the individuality of erbia. By fractionation of his material rich in erbia from alcoholic solution with an alcoholic solution of aniline, then of the middle portions of this series as earth chloride aniline hydrochloride by ammonia, he could not get an earth whose base had a constant atomic weight. The beautiful absorption spectrum of erbia was discovered by Bahr in 1862 (*Sv. Vet. Akad. Handl.*, 1862, p. 597; *Liebig's Ann. Chem.*, cxxxi., 256). Crookes (*CHEM. NEWS*, liii., 75) mapped all of the spectra of erbia. The absorption, emission, and spark spectra of thulia have been studied by Thalén (*CHEM. NEWS*, xlvii., 217; *Comptes Rendus*, xci., 376).

In 1883 Crookes (*Phil. Trans. Roy. Soc.*, clxiv., 89r; *CHEM. NEWS*, xlvii., 261; xlix., 159, 169, 181, 194, 205) discovered that the anhydrous sulphates of certain rare earths became phosphorescent when exposed to the electric discharge in a vacuum tube, and that this light gave characteristic spectra. He (*CHEM. NEWS*, xlv., 23; *Proc. Roy. Soc.*, xxxii., 209) had in 1881 observed that some of the earths themselves phosphoresced under the same conditions. In 1883 he discovered in these phosphorescence spectra the citron band which he decided to be due to yttria. In 1884, Lecoq de Boisbaudran (*Comptes Rendus*, c., 1437) discovered that if the positive pole were immersed in a solution of some of the rare earths, and the negative one brought just above its surface, the light which was emitted on the passage of the spark gave an inversion spectrum which was nearly related to the phosphorescence spectrum of Crookes. Both were very delicate, and were greatly influenced by the presence of foreign oxides.

In 1886 and the year following Crookes (*Journ. Chem. Soc.*, lv., 250; *CHEM. NEWS*, liv., 115; lv., 83, 95) separated yttria by a large number of different fractionations into five portions, each of which had different phosphorescence spectra, but all of which showed the spark spectrum of yttria. The bodies responsible for these phosphorescence spectra he called "meta-elements," and he developed his theory of the genesis of the elements on the basis of this observation. In further support of the idea that yttria was a complex substance, he stated that Marignac's gadolinia gave him the same phosphorescence spectrum as yttria, except that the citron band was missing, and that the two green bands of samaria were present. Then a mixture of 6r parts of yttria with 39 of samaria gave the same phosphorescence as gadolinia, except for the presence of the citron band. He also found that the yttria from different minerals gave phosphorescence spectra with its rays of varying intensity, showing that a partial separation had taken place in nature.

This theory and all its conclusions were opposed by Lecoq de Boisbaudran (*Bull. Soc. Chim.*, [3], iii., 53). He (*Comptes Rendus*, cii., 1536) showed that pure yttria gave no phosphorescence phenomena, either by his method or by that of Crookes. According to him, the fluorescence bands were attributable to impurities, to his substances Z_a and Z_β , in fact, and these it was almost impossible to remove completely from the yttria (*Comptes Rendus*, ciii., 113). In connection with these substances giving fluorescence bands, he (*Comptes Rendus*, cv., 258, 301, 343, 784; cx., 24, 67) has studied a considerable number of fluorescences with well-defined spectral rays, having for solid solvents alumina, gallium oxide, silica, zirconia, stannic and tantalic oxides, and for active matter samaria and the oxides of Z_a and Z_β . Demarçay (*Rev. Gen. des Sci. Pures et Appliquées*, i., 396; *CHEM. NEWS*, lxii., 85) opposed Crookes's theory of "meta-elements," and stated that the radiant matter test of Crookes was far more delicate than the reversion spectra of Lecoq de Boisbaudran.

Duboin (*Comptes Rendus*, cvii., 99) made some compounds of yttria in the dry way. The accepted atomic weight of yttrium, 89.02 with O = 16 as the standard, is the one obtained by Cleve in 1882 (*Comptes Rendus*, xcvi., 1225). Rowland (*CHEM. NEWS*, lxx., 68) published a method for the separation of yttria from other earths of its group by means of potassium ferrocyanide. His paper was severely criticised by Crookes (*CHEM. NEWS*, lxx., 81).

In 1896 Barrière (*CHEM. NEWS*, lxxiv., 159, 212) announced the existence, in the yttria earths from monazite, of a new metal which was separated from the other members of the group by precipitation with sodium thio-sulphate in concentrated solution. This element, lucium, had an atomic weight of 104. Crookes (*CHEM. NEWS*, lxxiv., 259), by examination of its spark and absorption spectra, found that it was a mixture of yttrium and didymium, erbium and terbium, but was principally yttrium. Shapleigh (*Journ. Franklin Inst.*, cxliv., 68; *CHEM. NEWS*, lxxvi., 41) found by a quantitative analysis

* *Journal of the American Chemical Society*, vol. xxiv., No. 5.

of a sample of lucia that it contained 93.98 per cent of yttria earths, 3.74 per cent of ceria earths, 1.07 per cent of thoria, and 1.21 per cent of other foreign oxides.

In 1896 and 1897 Schützenberger and Boudouard (*Comptes Rendus*, cxxii., 697; cxxiii., 782; cxxvi., 1648) worked on the yttric earths of monazite sands. They found by fractional fusion of the nitrates and by fractional crystallisation of the sulphates that a lower limit of fractionation was reached, giving an earth whose metal-equivalent (R_2O_3) was about 95. They thought that they had found a new earth, whose metal had an atomic weight of about 102. Drossbach (*Ber. d. Chem. Ges.*, xxix., 2452), working also on monazite, thought he had a new earth similar to the others (the atomic weight of its base, 100). Further, Urbain and Budischovsky (*Comptes Rendus*, cxxiv., 618), fractioning the yttria earths by means of the acetyl acetates, found a similar lower limit. Urbain (*Comptes Rendus*, cxxvi., 835; cxxvii., 107), working with the ethyl sulphates, succeeded in showing that this hypothetical earth could be separated into terbia ($R^{III} = 151.4$) at one end of his fractionation series and yttria ($R^{III} = 89$) at the other. In 1900 Urbain (*Ann. Chim. Phys.*, [7], xix., 184) again took up the question of this earth, and concluded that it was principally yttria, mixed with some erbia and terbia. This lower limit of various fractionation series, giving a base of nearly constant atomic weight, reminds one of the "oxide of gadolinium" of Nordenskiöld (*Comptes Rendus*, ciii., 795). This was a rare earth mixture, obtained from different minerals, which he knew to contain at least three oxides, those of yttrium, erbium, and terbium, and yet its metal had a constant atomic weight of 107.

Crookes (*CHEM. NEWS*, lxxviii., 134) in 1898 announced the existence of an element giving a group of phosphorescence bands in the ultra-violet only. He then called it monium. Its principal rays were λ 3120 and λ 3117, and its atomic weight about 118. In 1899, he renamed it victorium, and told how it was isolated (*Proc. Roy. Soc.*, lxx., 237; *Chem. Centrbl.*, 1899, II., p. 748). The method was a long combination of the standard ones of fusion of the yttria group nitrates, fractional precipitation of the oxalates from concentrated nitric acid solution, fusion of the nitrates again, and finally fractional precipitation with potassium sulphate.

In addition to all of these earths, and, of course, ceria, lanthana, didymia, and thoria, a few others have been announced. Their existence was generally short. Junonium was prepared in 1811 by Thomson from allanite (*Gilbert's Ann.*, xlii., 115; xliv., 113). Donarium was announced by Bergemann in 1851 (*Journ. Prakt. Chem.*, liii., 239). He prepared it by precipitating the silica-free acid solution of the mineral thorite with ammonia. Damour (*Pogg. Ann.*, lxxxv., 555), Berlin (*Pogg. Ann.*, lxxxv., 556; lxxxvii., 608), and finally Bergemann himself (*Pogg. Ann.*, lxxxv., 558) thought that donaria was identical with thoria. Bahr (*Pogg. Ann.*, cxix., 572; *Journ. Prakt. Chem.*, xci., 179) announced the discovery of wasium, which Nicklès (*Comptes Rendus*, lvii., 740) thought was a mixture of yttrium with didymium or terbia. Delafontaine (*Liebig's Ann. Chem.*, cxxxi., 364) thought wasium was cerium, perhaps with some didymium. Popp (*Liebig's Ann. Chem.*, cxxxi., 364) agreed with Delafontaine. Bahr (*Liebig's Ann. Chem.*, cxxxi., 227) considered it probable that wasium and thorium were identical, and that both Nicklès and Delafontaine were mistaken in the matter.

Smith (*Nature*, xxi., 146; *CHEM. NEWS*, xlix., 182) announced the existence of two new elements in samarskite, which he called columbium and rogerium. This columbium is not, of course, to be confused with the well-known one. Chroustchoff (*Berg. u. Huet. Zeit.*, xlv., 329; *Chem. Centrbl.*, 1887, p. 1277) detected spectroscopically the existence of a new element, russium, in certain wash residues from rocks, in many alumina preparations, and in American monazite. He (*Journ. Russ. Phys. Chem. Ges.*, xxix., 206; *Chem. Centrbl.*, 1897, xi., 329) prepared russium in much the same manner that Barrière prepared

lucium. Linnemann (*Monatsh. Chem.*, vii., 121) discovered astatium in the rare earth mixtures from orthite. Lecoq de Boisbaudran (*Comptes Rendus*, cii., 1436) considered it to be gallium. Pribram (*Sitzungsber. d. k. Akad. d. Wiss.*, Wien, Div. 2b, cix., 16; *Monatsh. Chem.*, xxi., 148) decided that Linnemann's product was gallium, at the same time maintaining the probability of a new element in orthite.

(To be continued).

NINETEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature, appointed by your body in 1882, respectfully presents its Nineteenth Annual Report, embracing the fourteen months from June 1, 1900, to August 1, 1901.

Works Published.

"A Select Bibliography of Chemistry, 1492-1897." By HENRY CARRINGTON BOLTON. Section VIII. Academic Dissertations. City of Washington: published by the Smithsonian Institution. 1901. 8vo. Pp. vi. + 534.

This forms No. 1253 of the Smithsonian Miscellaneous Collections, vol. xli.

This Bibliography of Academic Dissertations is a second part of the work published in 1893, and with the First Supplement, issued in 1899, completes (if the term can be applied to bibliography) the undertaking begun by Dr. Bolton in 1888. The three volumes comprise about 25,000 titles. The dissertations found in the libraries of the Smithsonian Institution and of the U.S. Geological Survey are indicated by appropriate initials. There is a full subject index.

The completed manuscript of a "Bibliography of the Analytical Chemistry of Manganese," by Professor Henry P. Talbot and John W. Brown, has been carefully examined by your Committee, and they have recommended it for printing to the Smithsonian Institution, to which it has been presented.

Works in Progress.

Mr. Frank R. Fraprie reports progress on his manuscript "Index to the Literature of Cæsium, Rubidium, and Lithium," which is to be completed within a twelve-month.

Mr. G. A. Smith, of Cornell University, reports that his "Index to the Literature of Selenium and Tellurium" will be completed by the close of the academic year.

Dr. M. D. Sohon is preparing for the press a "Subject-index to the Journal of the American Chemical Society."

Dr. H. Carrington Bolton has in preparation another "Supplement to the Select Bibliography of Chemistry," intended to cover the period beginning with 1897, and to include omissions.

Dr. Alfred Tuckerman has revised and prepared for the press the continuation of his "Index to the Literature of the Spectroscope"; the MS. has been presented to the Smithsonian Institution.

Notes.

During the past twelve months there have been published the following bibliographical works on chemical subjects:—

Bibliographia Lactaria. Bibliographie générale des travaux parus sur le lait et l'allaitement jusqu'en 1899. Paris, 1900. 600 pp. 8vo.

Bulletin de la Société Chimique de Paris. Tables des années 1899 à 1898, dressées par Th. Schneider. Paris, 1900. Two parts.

* Proceedings of the American Association for the Advancement of Science, 1901, vol. I.

Zeitschrift für physikalische Chemie, Stöchiometrie, und Verwandschaftslehre. Namen und Sach-Register über Band I.—xxv., bearbeitet von T. Paul, Leipzig, 1900. 8vo.

And Professor A. K. Krupsky, of St. Petersburg, announces a 62-page "Bibliography of Chemistry" in Russian, which your Committee is as yet unable to describe more accurately.

Committee:—

H. CARRINGTON BOLTON (in Europe),
F. W. CLARKE,
A. R. LEEDS,
A. B. PRESCOTT,
ALFRED TUCKERMAN,
H. W. WILEY.

THE INFLUENCE OF THE WATER PRESENT ON THE FLASH-POINT AND COMBUSTION-POINT OF PETROLEUM.

By J. MATUSCHEK.

WHILE examining a cloudy petroleum whose milky appearance was due to the presence of finely divided drops of water, I noticed with surprise that the flash-point, reduced to 760 m.m. pressure and 15° C., was between 23° and 24° C., and that the combustion-point was between 25° and 26° C. On shaking up 5 c.c. of this petroleum with an equal volume of sulphuric acid of 1.53 density the acid was observed to turn yellowish-brown, while a petroleum of good quality under the same conditions ought not to give more than a faint yellowish colouration.

It is well known that the presence of the bituminous products of distillation lowers both the flash-point and the combustion-point of a petroleum. We also know that in the presence of water the separation of the two liquids is fairly difficult, from which I have been led to the conclusion that the cause of high flash-points and combustion-points of petroleum was probably due to the proportion of water present.

To prove this supposition experimentally a petroleum was used whose density at 15° C. was 0.930.

The density of a petroleum of good quality should be from 0.79 to 0.82 at 15° C. When treated with sulphuric acid, as described above, this petroleum gave a brown colouration. On shaking up 5 c.c. of the petroleum with 2 c.c. of ammonia and a few drops of nitrate of silver, a brown colouration was produced, due to the reduction of silver by the sulphurised bituminous products. The flash-point and combustion-point, reduced to 760 m.m. and 15° C., were respectively 21° and 23° C. Fifty c.c. of this petroleum were then shaken up with 0.1 c.c. of distilled water until the mixture was homogeneous. The flash-point and combustion-point were then determined. The former was between 22° and 24° C., and the latter was 25° C.

Another 50 c.c. of the petroleum were then treated with 0.2 c.c. of water in the same manner, and the flash-point and combustion-point then obtained were respectively 27° C. and 29° C. With the addition of 0.3 c.c. of water 28° C. and 33.5° C. were obtained; 0.4 c.c. of water raised them to 30° C. and 34.5° C., 0.5 c.c. of water to 27° C. and 29° C., 0.6 c.c. of water to 28° C. and 30° C., and 0.7 c.c. of water to 30° C. and 32° C.

These facts show clearly that the proportion of water present in a petroleum contaminated with bituminous products of distillation raises the flash-point and the combustion-point of the petroleum; this increase depends on the quantity of water present.

The experiments show, further, that the regular rise of the flash-point and combustion-point is only maintained up to a certain degree; the regularity ceases as soon as small drops of water commence to form in the mixture during the experiment.

The formation of these small drops took place, in the last three experiments, within an hour at the ordinary temperature. After standing for twenty-four hours the first experiment only was still in the form of a homogeneous mixture.—*Österreich. Chem. Zeit.*, vol. iv., p. 209.

ANALYSIS OF TURF.

By H. BORNTAGER.

TURF of recent formation is of a relatively light colour and small density; it differs considerably from heavy dark turf, which is often several centuries old. They both contain the same constituents, but in different proportions. For example, in 100 parts of turf dried at 100° there are found:—

	Fibre.	Humic acid.	Nitrogen.
Light turf	95—90	5—10	0.5—1.0
Heavy turf	58—48	40—50	2.0—2.5

Light turf absorbs a large quantity of water, while heavy turf hardly absorbs any at all. The French methods of analysis take no notice of any difference between fibre and humic acid, and the author is of the opinion that it is important to estimate these substances separately when dealing with a turf required for agriculture or distillation.

In an analysis of turf destined for these uses the following are determined:—

1. *Moisture*.—A finely divided portion is dried at 100° until the weight is constant. The quantity varies between 10 and 40 per cent.
2. *Mineral Wax*.—The dried turf is extracted with anhydrous ether; the results vary from 0.5 to 1.0 per cent.
3. *Nitrogen*.—By Kjeldahl's method we generally find from 0.5 to 2.5 per cent. About half the nitrogen is present in the form of ammonia, which can be estimated by boiling 1 part of the turf with a concentrated solution of caustic soda, and collecting the ammonia given off in titrated acid.
4. *Humic Acid and Fibre*.—One or 2 grms. are extracted three times by boiling for an hour with 5 grms. of soda and 200 grms. of water; the extracts are filtered on a tared filter. After washing, the residue is dried at 105°; this represents the fibre. The humic acid is then estimated in the alkaline filtrate.
5. *Ash*.—About 1 gm. is incinerated with nitrate of ammonium in a platinum crucible without a cover. The proportion varies from 2 to 10 per cent.

French analyses give the principal constituents of the ash; that is to say, the insoluble matter, the lime, magnesia, potash, and phosphoric acid; but in the author's opinion these estimations are of little importance. There is also a rapid method for the estimation of humic acid alone, already described by the author and M. Tacke (*Chem. Zeit.*, 1896, p. 23; and 1893, p. 174). A known weight of turf is boiled with a finely powdered carbonate, the carbonic acid given off is estimated and the quantity of humic acid present is deduced by calculation.

The following are typical analyses made by the author's method:—

	Light turf from Hanover.		Heavy turf from Aldenbourg.	
	I.	II.	III.	IV.
Water	30.0	29.0	20.0	20.0
Ash	3.0	3.1	2.8	3.0
Fibre	55.0	54.9	49.0	47.0
Humic acid	12.0	13.0	38.0	30.0
Total	100.0	100.0	100.0	100.0
Total nitrogen	1.1	1.3	1.8	2.0
Nitrogen as ammonia	0.3	0.4	0.6	0.7

Turf intended for use as fuel should naturally have its calorimetric power estimated.—*Zeit. Anal. Chem.*, 1901.

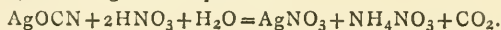
ANALYSIS OF COMMERCIAL CYANIDES.

AN EXACT METHOD FOR THE DETERMINATION OF CYANIC ACID; A DOUBLE CYANIDE; AND AN ANTIDOTE FOR CYANIDES.

By O. HERTIG.

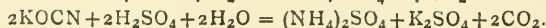
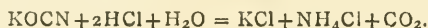
THE use of cyanide of potassium and cyanide of sodium for the extraction of gold is constantly increasing. The attention of manufacturers is therefore directed to the most economical methods possible for the preparation of these salts, and to all industries in which they are obtained as by-products—I need only instance the manufacture of lighting gas. Analysts have also been engaged in devising more exact and more rapid methods for the estimation of cyanides.

First of all, there is M. Mellor's work (*Zeit. Anal. Chem.*, vol. xl, p. 17) on the determination of cyanides and cyanates. The author recommends nitrate of calcium to precipitate the carbonates which are always present in small quantities. Nitrate of barium, recommended by Holdenauer (Lunge, "Chem. Tech. Untersuchungs-methoden," vol. i., p. 438), is rejected; cyanate of barium is, in fact, insoluble in water. In so far as the determination of cyanogen in cyanides is concerned, M. Denigès's method, recommended by Mellor, is certainly the best and most convenient. The method of Fordos and Gelis (Lunge, *loc. cit.*, vol. i., p. 489) always gives too high results. But the method of Mellor and Allen for the determination of cyanic acid cannot be approved of. This titration with nitric acid, followed by a back-titration with soda, gives very different results to those obtained by other methods. It seems that the temperature at which the mixture of cyanide and cyanate of silver is to be digested, 50° (for how long?), is not high enough. It would appear to be preferable to let the nitric acid act on the cyanate of silver for an hour at the temperature of the water-bath. It must also be remembered that the filtrate which is titrated back with soda contains an ammoniacal salt, according to the equation—



Still, analyses I have made do not enable me yet to pronounce a definite opinion on this method.

The method of estimation I propose is based on a determination of the nitrogen, and on the decomposition of the cyanates by hydrochloric or sulphuric acid. This decomposition gives rise to an ammoniacal salt, as shown in the following equations:—



To determine the cyanic acid in the cyanides we take 0.2 to 0.5 grm. of material. This is dissolved in a few c.c. of water, and treated in a porcelain crucible with dilute hydrochloric or sulphuric acid; it is then evaporated to dryness on the water-bath and taken up with water. The ammonia is estimated in this solution by boiling with soda and collecting the gas which escapes in 1/5th N sulphuric acid. After the operation the acid is re-titrated with 1/5th N ammonia, using fluorescein as an indicator. The presence of chloride of ammonium may lead to errors if we estimate the potassium with chloride of platinum after having decomposed the cyanates with hydrochloric acid. When we wish to estimate the potassium, it is necessary, after decomposing the cyanates by hydrochloric acid in a platinum crucible, to drive off the chloride of ammonium by calcination. It must not be heated beyond a dull red, or there would be a risk of decomposing the chloride of potassium.

I have recently had a sample of cyanide containing 38.85 per cent of cyanogen (pure cyanide of potassium contains 40 per cent of CN and 60 per cent K). Now, the proportion of potassium was 31.45 per cent, and that of the nitrogen 15.83 per cent.

The complete analysis gave the following results:—

	Per cent.
Insoluble part (SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃)	0.03
NH ₄	0.33
K	19.23
CN	31.45
CO ₂	38.85
CNO	2.94
O (calculating CO ₂ into K ₂ CO ₃)	2.65
OH	2.93
Cl	0.44
Total	99.91

The question was, acting on these results, to determine the composition of the substance. By treating a sample of the material with warm alcohol, a residue of carbonate of potassium was obtained. The proportion of OH, obtained by nitrate of magnesium, could only be in combination with the potash, and not the ammonia. It must be admitted also that the cyanic acid was united with the potash, as the ammoniacal solutions of this acid decompose rapidly, while the solution of the substance under examination remained for several days without change. From the above it would appear that we had to deal with a double cyanide of potassium and ammonium of the composition:—

	Per cent.
Insoluble part	0.03
Moisture	0.33
NH ₄ CN	46.98
KCN	27.72
K ₂ CO ₃	9.22
KCNO	5.06
KOH (corresponding to 2.93 per cent OH, instead of 3.16 per cent)	9.65
KCl	0.92
	99.91

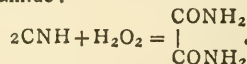
I ought to say that the figure 3.16 per cent was obtained with the nitrate of magnesium method; this figure is rather too high. The figure 2.93 was found by calculating the potassium remaining into potash.

This double cyanide of potassium and ammonium occurs in pure white amorphous fragments having a strong odour of hydrocyanic acid. When calcined in an open crucible, it increases in weight; this is due to the formation of a cyanate. Its aqueous solution remains unchanged for several days, and no azulinic acid is formed (C₄H₅N₅O).

It cannot be decided with any certainty whether this salt is suitable for the extraction of gold from tailings without making experiments on an extended scale. Neither can I describe the manner of preparation of this compound.

The question of an antidote for hydrocyanic acid is always of importance, considering how the use of cyanides is increasing. It has been solved by M. Robert and his pupil, M. Krohl. On this point I would call attention to "Merck's Annual Report for the Year 1899"; it recommends the use of peroxide of hydrogen as an antidote for cyanides. A 30 per cent solution is administered for internal use, and a 3 per cent solution for subcutaneous injections.

Peroxide of hydrogen transforms hydrocyanic acid into a harmless oxamide:—



For the past three years this method has been used successfully in cases of poisoning by cyanide in English mining districts (*Journal of the Chemical and Metallurgical Society of South Africa*, 1899). It would be advisable, therefore, to insert this treatment by peroxide of hydrogen in the various publications which are met with under the general title of "First Aid to the Injured." In

the greater number of these cases of poisoning, it was only inhalation of prussic acid fumes which had occurred, and every chemist or foreman can easily learn how to administer a subcutaneous injection.—*Zeit. für Angew. Chemie*, 1901, p. 619.

ON A MODIFICATION OF ROSE'S METHOD OF SEPARATING COBALT AND NICKEL.*

By R. L. TAYLOR, F.C.S.

NUMEROUS methods have been proposed for the purpose of separating cobalt and nickel when in solution together. The two metals, however, are so much alike in their general properties, that very few methods appear to give satisfactory results, and those few are, as a rule, troublesome and tedious.

The method which I have described as "Rose's method" was proposed by him over fifty years ago (*Pogg. Ann.*, Bd. 71, p. 545), and a translation of Rose's paper, by T. H. Henry, appeared in the *Chemical Gazette* for 1847, page 362, accompanied by some remarks on the method by the translator. The process, while fairly satisfactory, was very tedious and troublesome, and probably for that reason, it appears to have gone out of use. It is described in "Gmelin's Handbook," and in various editions of Fresenius's "Quantitative Analysis" but very few modern text-books even mention the reaction (which is interesting and important) upon which the method depends. For example, it is not referred to in Roscoe and Schorlemmer's "Treatise on Chemistry," and there is no mention of it in the newer Watts' "Dictionary of Chemistry."

Rose's method depends upon the fact that cobalt is precipitated as the black sesquioxide by various insoluble carbonates (such as those of barium, strontium, and calcium) in presence of free chlorine or bromine, and that nickel is not so precipitated. The following equation practically represents what takes place in the case of cobalt:— $2\text{CoCl}_2 + 3\text{BaCO}_3 + \text{Cl}_2 = \text{Co}_2\text{O}_3 + 3\text{BaCl}_2 + 3\text{CO}_2$. It is very probable, however, that the cobalt is converted from a cobaltous to a cobaltic salt before it is precipitated by the carbonate.

According to his original description of the process, Rose passed a stream of chlorine through a somewhat dilute solution of the chlorides of the two metals, containing a considerable excess of hydrochloric acid, for several hours. He then added excess of barium carbonate and allowed to stand, with frequent agitation, for from twelve to eighteen hours. By the end of that time the cobalt was all converted into sesquioxide, and the nickel remained in solution, and could be filtered off. In his remarks on Rose's method (referred to above) Henry suggested the use of bromine instead of chlorine. In a subsequent letter (*Chem. Gazz.*, 1855, p. 237), Henry stated that he had, by keeping the temperature at 120° F., succeeded in reducing the time required to a few hours. He considered that the results, however, were not so good as those obtained by Liebig's method of separation by means of potassium cyanide.

Induced principally by a desire to find a better method than those usually employed for the qualitative separation and detection of nickel in presence of cobalt, I have recently made some experiments on the action of barium and calcium carbonate on solutions of the two metals, in presence of chlorine and bromine. As the result of these experiments, I find that the method of Rose can be considerably shortened, with the result also of making it much more accurate.

The mistake which both Rose and Henry made was in the use of free hydrochloric acid before the addition of chlorine (or bromine) and the carbonate. Rose mentions

having tried a neutral solution, but with unsatisfactory results. On the other hand, I find that if there is *no* free acid present, barium or calcium carbonate, in presence of chlorine or bromine, will precipitate cobalt completely in three or four minutes. Perhaps barium carbonate acts a little more rapidly than calcium carbonate, but, in a great many experiments I have made, neither of them has ever failed to precipitate the cobalt in five minutes.

With a neutral solution of nickel, on the other hand, I have never found any precipitation of the black oxide within an hour. After a longer time, a black deposit begins to form on the side of the vessel at the edge of the liquid, where the air has access to it. If air is excluded nickel scarcely appears to be precipitated at all. I have had solutions of nickel in presence of both barium and calcium carbonate and bromine water in stoppered bottles for some weeks without any appearance of precipitation of the black oxide. When the liquid is heated to a temperature of 70° or 80° C., the nickel is rapidly precipitated as the black sesquioxide.

If, however, much free acid is present when the carbonate and bromine water are added, as was always the case in following Rose's original method, the precipitation of the cobalt is very considerably retarded. It may take hours, and sometimes does not even begin for over half-an-hour. This explains why Rose found it necessary to allow his solutions to stand so many hours.

The retarding effect of the free acid is rather surprising, because all free acid naturally becomes neutralised by the carbonate employed, which must always be in excess. My first impression was that the soluble barium or calcium salt formed when the acid is neutralised by the carbonate must be the cause of the retardation, but experiment showed that it was not. The cause of the retardation is simply free carbonic acid. If, after adding the carbonate to a solution of cobalt containing free acid, the liquid is boiled (to expel the carbon dioxide) and cooled again before adding the bromine water, there is no retardation. Also, if carbon dioxide is bubbled through a neutral solution of cobalt, or if such a solution is mixed with ordinary soda-water, on adding the carbonate and bromine water there is a retardation of the precipitation of the cobalt similar to that observed when free acid is present at the outset.

This curious retarding action of free carbonic acid appears additionally strange when it is borne in mind that carbon dioxide is one of the products of the reaction itself, and that immediately the reaction begins there must be free carbonic acid present in the liquid. Plainly, the retarding action of the free carbonic acid is very slight unless there is a considerable amount of it in proportion to the water, and in dilute solutions the amount never becomes sufficient. In *strong* neutral solutions the carbonic acid produced during the reaction has its effect, and the precipitation of the cobalt takes much longer. At present I am unable to suggest any reason why free carbonic acid should exert this curious retarding effect.*

With a dilute solution which is approximately neutral the process of separation works rapidly and well. I have tested it quantitatively with most satisfactory results. The materials I used were the crystallised chlorides of the two metals, each guaranteed by the makers as free from the other.

A solution of chloride of nickel was prepared, of no definite strength, and the amount of nickel in it was determined by electrolytic deposition, from an ammoniacal solution, on a weighed platinum basin—a process of estimating nickel which appears to be most satisfactory. In this way, in two separate experiments 50 c.c. of the solution gave 0.1350 and 0.1355 grms. of metallic nickel respectively. In two further experiments, 50 c.c. of the same solution were mixed, in each case, with an indefinite

* It is well known that manganese is precipitated by barium or calcium carbonate under the same circumstances as cobalt, and I find that free carbonic acid acts exactly as it does with cobalt—the precipitation of the manganese is very considerably retarded.

* A Paper read before the Manchester Literary and Philosophical Society, February 18, 1902.

amount of a solution of cobalt. The two metals were then separated by adding excess of precipitated barium carbonate, made into a paste with water, and bromine water. Ten minutes were allowed for the precipitation of the cobalt. After filtering and washing, the barium was removed from the filtrate by precipitation with sulphuric acid, the liquid evaporated to a small bulk, and the nickel determined by electrolytic deposition. The two experiments gave respectively 0.1345 and 0.1347 grms. of nickel.

In a similar way a solution of chloride of cobalt was prepared, and the amount of cobalt in it determined by electrolytic deposition from a solution of the double oxalate of cobalt and ammonium, this being one of the solutions of cobalt which is said to give the best results. But, in my hands at any rate, the process of electrolytic deposition is not so satisfactory with cobalt as with nickel. The deposited metal is not so clean, and it is difficult to know when the process is complete. Thus, in one experiment 50 c.c. of the solution of cobalt, electrolysed for five hours (when the deposition seemed to be complete), gave 0.1517 grm. of metallic cobalt. In another experiment, when the electrolysis was carried on through the night (altogether about seventeen hours) 50 c.c. gave 0.1537 grm. of cobalt. Possibly the larger amount represents the true strength of the solution.

Mixtures were next made of 50 c.c. of each of the two solutions, the separation effected as before, and both the cobalt and nickel determined electrolytically. In one experiment, where the electrolysis of the cobalt solution was allowed to proceed throughout the night, 0.1542 grm. of cobalt and 0.1352 grm. of nickel were obtained. In another, where the cobalt solution was electrolysed for seven hours, the numbers were 0.1532 and 0.1347 respectively.

In addition to the above results obtained by myself, some experiments on this method of separation have been made by Mr. David Segaller, A.R.C.S., Dublin, with equally satisfactory results.

The above results are very much better than those quoted by Rose and Henry for the original method. This may be due to the fact that my materials were probably purer than any they were able to obtain. The results demonstrate quite satisfactorily that by this method the separation of cobalt and nickel is not only rapid, but complete.

The process not only acts well quantitatively, but I recommend it very strongly for the separation and detection of cobalt and nickel in the ordinary process of qualitative analysis. The mixed sulphides of cobalt and nickel are dissolved in the usual way in dilute hydrochloric acid with the aid of a crystal of potassium chlorate. The liquid is then boiled down just to dryness in order to expel the free acid. The residue is taken up with water, and precipitated barium or calcium carbonate and bromine water added.* It is now allowed to stand for five minutes, with frequent shaking. If cobalt is present, a black precipitate very soon appears. At the end of five minutes the liquid is filtered, and the filtrate tested for nickel by the addition of a drop or two of ammonia and ammonium sulphide. The presence of cobalt in the precipitate may be confirmed by the borax bead test. In this way nickel may be detected even when present in very small quantity, and when the cobalt is largely in excess.

Instead of boiling off the free acid, it may be neutralised with sodium or potassium hydrate before adding the carbonate and bromine water; or the carbonate of barium or calcium may be added in excess to the acid liquid, and then the liquid boiled for a short time to expel the free carbon dioxide. It must then be cooled to the ordinary temperature before adding the bromine water.

The carbonates of barium, strontium, and calcium are not the only ones which act in the manner described; the

carbonates of magnesium and zinc apparently act in the same way. Thomas Moore (CHEM. NEWS, 1900, vol. lxxxii., p. 73), describes the use of zinc oxide and bromine water for the purpose of estimating small quantities of cobalt in presence of nickel. Mr. Moore finds that those reagents precipitate cobalt as sesquioxide, but not nickel, even on boiling. He insists that bromine *must* be used, and not chlorine. I have tried the experiment, and fail to find any difference at all between the action of chlorine and bromine.

ZIRCONS FROM CEYLON.

ILLUSTRATING RANGE AND CHANGE OF DENSITY AND COLOUR.

Exhibited by Prof. A. H. CHURCH, D.Sc., F.R.S., at the Royal Society Conversazione, May 14, 1902.

ZIRCONS, GREEN.—Range of density, 4.0 to 4.19; raised by heating from 4.0 to 4.31, from 4.11 to 4.51, from 4.19 to 4.39, and from 4.19 to 4.57. These almost alone amongst zircons emit a brilliant orange light during grinding with diamond dust. This phenomenon does not occur with these stones after their density has been raised by strong heating.

ZIRCONS, GOLDEN.—Range of density, 4.38 to 4.45; raised by heating to 4.66. These zircons continuously glow with an orange incandescence in the flame of a Bunsen burner.

ZIRCONS, YELLOW.—Range of density, 4.6 to 4.64; raised by heating to 4.7, the colour being sometimes lost completely.

ZIRCONS, RED.—Range of density, 4.67 to 4.71, unaltered by heating, but the colour reduced.

The molecular volume of zirconia, if normal, would correspond to a density in zircon of 4.0, and would then be in accord with the molecular volumes of the other bin oxides belonging to Mendeleeff's Group IV.

The contraction suffered by certain zircons when strongly heated was first observed by Henneberg in 1846. It was more fully studied by Damour in 1864 and by the Exhibitor in the same year. In one of the instances shown it corresponds to a reduction of volume from 100 to 91.3.

The striking absorption spectrum of certain zircons is shown in a careful drawing by Dr. C. A. MacMunn. This spectrum (first observed and published by the Exhibitor in 1866) has not before been accurately mapped, although Becquerel gave the wave-lengths of the several bands in 1888. Dr. MacMunn's measurements for the darkest parts of eleven bands are:—

λ	λ
689.5	589.0
683.5 (not shown in the drawing)	562.0
661.0	538.0
653.0	515.0
622.5	484.0
616.0	

Tellurium-diphenyl and the Atomic Weight of Tellurium.—O. Steiner.—The author first prepared telluride of phenyl according to the method of MM. Krafft and Lyons, by heating 36.5 grms. of pure powdered tellurium with 50 grms. of mercury-diphenyl in a sealed exhausted tube at a temperature of 220–230° for fifteen hours:— $(C_6H_5)_2Hg + 2Te = (C_6H_5)_2Te + HgTe$. The contents of the tube are exhausted with ether and filtered to separate the $HgTe$, and a brown oil is collected; this can be rectified at a pressure of 100 m.m. Thus an oil is obtained which is again heated for three hours at 200° with 5 grms. of powdered tellurium. This is again rectified *in vacuo*, and then once more over copper turnings. Finally, a highly refracting oil is obtained, boiling at 174° and 100 m.m., and at 110–112° *in vacuo*. The analysis of this product, $(C_6H_5)_2Te$, carried out on different portions, give for $O = 16$ at the ordinary pressure, $Te = 126.4$ to 126.7.—*Berichte*, vol. xxxiv., p. 570.

* Barium and calcium carbonates appear to act equally well. The dry substances may be employed. Barium carbonate is preferable if the subsequent removal of the added metal is desired.

THE
RADIO-ACTIVITY OF THORIUM COMPOUNDS.

I. AN INVESTIGATION OF THE RADIO-ACTIVE
EMANATION.

By E. RUTHERFORD, M.A., D.Sc.,
Macdonald Professor of Physics, McGill University, Montreal,

and
FREDERICK SODDY, B.A. (Oxon.),
Demonstrator in Chemistry, McGill University, Montreal.

THE following paper contains a preliminary account of an investigation into the property possessed by the compounds of thorium of giving a radio-active emanation, and also into the nature of the emanation itself.

It was shown by one of us (*Phil. Mag.*, 1900, [5], xlix., i., 161) that the compounds of thorium, besides being radio-active in the same sense as the uranium compounds, also continuously emit into the surrounding atmosphere, under ordinary conditions, something which, whatever its real nature may be, behaves in all respects like a radio-active gas. This "emanation," as it has been named, is the source of rays, which, like the Röntgen and uranium rays, and the ordinary well recognised type of thorium radiation, will darken a photographic plate, and will render a gas capable of conducting an electric current (that is, will "ionise" it), but is sharply distinguished from them by the following considerations. It can be moved from the neighbourhood of the thorium compound by a current of air passing over it, or even by the process of ordinary gaseous diffusion, and transported long distances, so that the characteristic photographic and ionisation effects appear in the air far away from the original source of radio-activity. The Röntgen and uranium rays, as is well known, travel in straight lines from their source, and any object opaque to them interposed in their path will sharply screen the space behind. But in the case of the thorium radiation there is no such screening effect, because here we have a case of a substance emitting, not only straight line radiation, but also particles of a gas, itself radio-active, capable of diffusing through the surrounding atmosphere around obstacles placed in its direct path, and so arriving and producing its effects at points completely screened from rays travelling from the thorium in straight lines. It was shown in the original communication that these effects could not be ascribed to minute particles of thorium dust carried off mechanically, and all the subsequent work on the subject shows that the hypothesis that the compounds of thorium emit a radio-active gas is not merely the only one which will explain the facts, but that it does so in every observed case in a completely satisfactory manner.

Present State of the Subject from a Physical Standpoint.

In the papers referred to, the general character of the phenomena in question was presented, and a short *résumé* will perhaps not be out of place here. It was shown that the radiation from the emanation decays rapidly, but at a perfectly defined rate; that is, the effects it produces diminish with the lapse of time, falling to about one-half the original value at the end of one minute. This "rate of decay," as will be shown later, is of great value in identifying and distinguishing between different types of emanation.

The emanation passes unchanged through cotton-wool, weak and strong sulphuric acid, and aluminium and other metals in the form of foil, but not through an extremely thin sheet of mica.

The emanating power of thorium is independent of the surrounding atmosphere, but is destroyed to a large extent by intense ignition, and does not return when the substance is kept.

One of the most striking properties of the thorium emanation is its power of exciting radio-activity on all surfaces with which it comes in contact; that is, a substance after being exposed for some time in the presence of the

emanation behaves as if it were covered with an invisible layer of an intensely radio-active material. If the thorium is exposed in a strong electric field, the excited radio-activity is entirely confined to the negatively charged surface. In this way, it is possible to concentrate the excited radio-activity on a very small area. The excited radio-activity itself has a regular rate of decay, but different from that of the emanation, its effect falling to half value in about eleven hours. There is a very close connection between the excited radio-activity and the emanation. It was shown that the amount of the former produced under various conditions was proportional to the amount of the latter, and if the emanating power of thorium be destroyed by intense ignition, its power to excite radio-activity correspondingly disappears. Some apparent discrepancies which at first stood in the way of too close a connection being inferred have resolved themselves by recent work into strong confirmation of the view that the two are related to each other as cause and effect.

Another remarkable property of the excited radio-activity is that it is soluble in sulphuric and hydrochloric acids; that is, a platinum wire, rendered radio-active by being made the negative pole of an electric field in the neighbourhood of some thorium, will give up its radio-activity to these acids. If the acid be then evaporated, the radio-activity remains on the dish, whilst if left to itself the radio-activity of the acid solution decays at a rate identical with that of the original excited radio-activity on the platinum wire.

Simultaneously with the discovery of excited radio-activity due to thorium, Curie showed that radio-active barium possessed a similar property. Later, Dorn (*Abh. der Naturforsch. Ges. für Halle-a-S.*, 1900) repeated the work quoted for thorium, and extended it to include two preparations of radio-active barium compounds (radium) prepared by P. de Haen, and a preparation of radio-active bismuth (polonium). He found that radium gave out an emanation which was similar to that from thorium, but which retained its radio-active power much longer. The excited radio-activity from radium, on the other hand, decayed more rapidly than that from thorium. The special property of emitting an emanation is, however, confined to the compounds of radium and thorium, those of uranium and polonium do not possess it to an appreciable extent.

An approximate determination of the molecular weight of the emanation produced by radium has been carried out (Rutherford and H. T. Brooks, *Nature*, 1901, lxi., 157) by a diffusion method, taking advantage of the slow rate of decay of the radium emanation. From comparison of the rate of diffusion of gases of known molecular weight into one another, it was found that the molecular weight probably lies between 40 and 100.

It seemed probable that an examination of the phenomena by chemical methods might throw light upon its nature, and the emanation produced by thorium was chosen as more suitable for the purpose than that produced by radium, on account of the obscurity still surrounding the chemistry of the latter, and the difficulty of producing material of even approximate uniformity of properties. Thorium, on the other hand, is an article of commerce, and specimens from different sources show surprising uniformity in this respect.

During the progress of the work, the subject has acquired additional importance and interest through the discovery by Elster and Geitel (*Phys. Zeit.*, 1901, ii., 590) that it is possible to produce excited radio-activity from the atmosphere, without further agency, by simply exposing a wire highly charged to a negative potential in the atmosphere for many hours, and that this also possesses the property of being dissolved off by acids, and of being left behind unchanged on the evaporation of the latter. But here again the rate of decay is different from that of the excited radio-activity produced by thorium, which is evidence for assuming that the two are probably not identical, although so strikingly analogous. However, the

close connection between excited radio-activity and the emanation established in the case of thorium renders it probable that the excited radio-activity obtained from the atmosphere is caused by the presence there of an emanation or radio-active gas analogous to, although probably different from, the thorium emanation. The discovery is likely, as Elster and Geitel point out, to have important bearings on the theory of atmospheric electricity, and in our opinion renders a close study of the thorium emanation the more imperative.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 23rd, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

MR. T. C. PORTER showed A Lecture Experiment on the Ebullition of Rotating Water.

If the water in a beaker, having approximately vertical sides, be caused to rotate about an axis concentric with the vertical geometrical axis of the beaker, it is obvious that in any horizontal section of the water the pressure is least in the centre and increases from the centre outwards. If the temperature of the water is just below boiling-point and heat is supplied to it whilst it is rotating, steam is formed only in the region of least pressure, and a gaseous core is produced. The rotation can be given to the water by stirring it with a glass rod covered with a piece of india-rubber tubing, and maintaining the stirring motion during the act of withdrawal of the rod. Some curious phenomena are shown by the column of steam, if the water is first stirred and then left to come to rest whilst the heating is continued. At first there is a markedly concave surface to the water in the beaker, and the column of steam is practically continuous from base to summit. After this stage pulsations set in. The course of events during a single pulsation is as follows:—1st phase, the surface of the water flattens, and when most nearly level a column of steam springs up with great rapidity from the base of the beaker to the surface of the water, heaving this up in its central portion. Immediately after the eruption of the steam, and whilst the column still stretches from the base of the beaker to the surface of the water, follows the second phase. The steam column seems to condense, and breaks up, leaving only a few small bubbles, which either hang stationary or move downwards in the liquid; whilst if the water has dust in it, the motion of the dust particles shows that a curious kind of annular wave, concentric with the steam column, traverses the water from top to bottom, apparently causing in its course the almost complete condensation of the steam, and the curious brief downward movement of the bubbles left. At the same time the surface of the water in the beaker becomes deeply indented. After this the apex of the surface vortex rises, and the first phase of the phenomenon recurs. The curve of the surface of the water throughout is never a parabola, the divergence indicating that the water rotates more rapidly as it nears the axis. The pulsations can also be produced by stirring cold water in a beaker-shaped jar, having a small hole in its bottom through which a stream of air-bubbles can be blown. The forms of the steam columns in some cases present a likeness to those of solar prominences; and Mr. Porter suggested that the immediate cause of the latter might be the diminution of pressure on the sun's surface at, or near, the centre or centres of depressions caused by violent cyclonic disturbances in the solar atmosphere. He asked for an explanation of the pulsations.

Mr. C. V. BOYS exhibited a small Heat Engine in which rotating water evolved steam without ebullition.

MR. T. H. BLAKESLEY expressed his interest in the apparent want of buoyancy of the steam-bubbles in the second phase of the pulsation. He said that in filtering liquids he had sometimes noticed what appeared to be large bubbles of air which lacked buoyancy. They were really drops of the liquid surrounded by a film of air. He suggested that the curve of the water surface could be made parabolic by rotating the beaker. In this case the vertical distance between the highest and lowest points of the surface would be a measure of the velocity of rotation.

MR. W. WATSON said that as the viscosity of water changed rapidly when nearing the boiling-point, small variations in the temperature of the liquid might alter the parabolic form of the surface. Any bubbles of steam formed away from the axis of rotation would be driven to the axis on account of the greater density of the water.

MR. PRICE said he had seen some similar experiments illustrating the formation of water spouts. The appearance was like the effect shown, but the pulsations were absent.

DR. A. GRIFFITHS, in suggesting an explanation of the oscillation of the water, pointed out that if the distance of a rotating body (held in position by a spring) from the axis be forcibly diminished, the conservation of the moment of momentum indicates an increased rate of rotation. On releasing the body, the increased centrifugal force causes it to shoot past its original position. Beyond the position of equilibrium, the conservation of the moment of momentum indicates a diminished speed which decreases the centrifugal force. Thus the body oscillates radially. When the water in the beaker is flat, the mass of the water is at a less average distance from the axis of rotation than when it is heaped towards the sides. Thus the outward-driving force is probably larger when the depression is small than when it is large. The outward force drives the water beyond the position of equilibrium which it would hold in the absence of oscillation.

THE CHAIRMAN said it would be interesting to observe the effects produced by varying the method of supplying the heat to the water.

A paper by Mr. J. A. ERSKINE, on "*The Conservation of Entropy*," was read by the SECRETARY.

Heat energy may be expressed as the product of two factors—a quantity factor, entropy, and an intensity factor, temperature. The conservation of entropy holds in thermodynamics when dealing with reversible processes, and is analogous to the conservation of other quantity factors such as momentum, moment of momentum, and electric quantity. The author shows the completeness of the analogies by considering Carnot cycles carried out on electrostatic and hydraulic engines. Prof. Wiedeburg has proposed to extend the doctrine of the conservation of entropy to irreversible processes by introducing a new quantity analogous to electric resistance.

THE SECRETARY read a letter from Mr. SWINBURNE, in which he stated that the author had got hold of what was no doubt Clausius's original idea of entropy. The science of thermodynamics, as far as it deals with reversible processes, depended upon what the author called the conservation of entropy, but reversible processes did not exist in practice. The author's treatment was quite in accordance with orthodox thermodynamics.

A paper by Sig. G. GIORGI, on "*Rational Units of Electromagnetism*," was read by Mr. PRICE.

MR. PRICE prefaced the reading of the paper by saying that both Prof. Fleming and Prof. Fessenden had advocated a partial change of units which would leave the most important ones unchanged, and the method employed by the author was similar to that adopted by Prof. Fessenden. The author starts with a set of three equations, which contain explicitly the four concrete units of E.M.F., M.M.F., electric current, and magnetic current, together with that of activity, and considers them as fundamental in electromagnetism. Two fundamental units are required to express these quantities, and their product must reproduce the mechanical unit of activity. If the watt is assumed as

unit of activity, there are two units ready made, the volt and the ampère, which satisfy the condition, and may be considered fundamental. All concrete units in electricity and magnetism can be expressed in terms of these and the second as unit of time. In order to complete the system, a unit of length is required. The metre and kilogramme are consistent with the watt, and putting them together with the units enumerated in the paper, the author has built up an absolute metre-kilogramme-second system which comprises electric, magnetic, and mechanical measures in a consistent frame.

The SECRETARY read a letter from Mr. SWINBURNE stating that: most physicists who love simplicity would be glad to get rid of "4 π ," but schemes for suppressing it generally moved it somewhere else. He asked if the author had really got rid of 4 π or merely chained it up in another place. If a change in units were to be made, it would be an advantage to get rid of the terms electromotive force and magnetomotive force.

Prof. EVERETT said he had arrived at the following determinations of the author's meaning:—

When μ and K are taken into account, we have the two following identities:—

1. The dimensions of current are the same as those of magnetomotive force, or $H \times \text{length}$, called f in the paper.
2. The dimensions of electromotive force are the same as those of quantity of magnetism divided by time—called by the author magnetic current, and denoted by g .

In connection with 1, the line-integral of H for a path singly linked with a circuit carrying a current of C ampères is to be called C . This gives the unit for H in terms of the ampère and the unit of length (the metre).

In connection with 2, we are to use the equation for magneto-electric induction in a circuit

$$\text{electromotive force} = - \frac{dN}{dt},$$

together with the rule that a quantity of the magnetism m gives the total flux $N = m$. The unit quantity of magnetism is thus defined in terms of the volt and the unit of time (the second).

The CHAIRMAN said he had received a paper from Sig. Giorgi, giving a number of illustrations of the application of his theory to calculations. There were also some further explanations, and the dimensions of many physical quantities were tabulated in terms of the volt, ampère, and second. The author claimed to have based an absolute system on the metre, kilogramme, and second, while leaving the practical units unchanged.

The Society then adjourned until June 13th.

The Preparation of Chlorine by means of Chlorate of Sodium, and the Preparation of Trichloride of Phosphorus.—C. Graebe.—To prepare chlorine, hydrochloric acid, $D = 1.1$ (or on the large scale $D = 1.2$), is heated to incipient boiling, and by the aid of a stoppered funnel with a long thin stem a fine stream of commercial chlorate of sodium at 500 grms. per litre is run in. The gas is thus given off at about 200°, and only contains very small quantities of peroxide of chlorine, which in this proportion is without objection for the ordinary uses of chlorine. It can, however, be removed if so desired by means of a wash-bottle, ClO_2 being more soluble in water than chlorine is. To prepare the trichloride of phosphorus, chlorine is passed into a flask containing red phosphorus under a layer of PCl_3 prepared previously. The tube carrying the chlorine plunges into the PCl_3 close to the phosphorus, and is arranged in such a manner that by the aid of a stirrer the end can be cleared if it becomes obstructed by a deposit of PCl_5 . The flask is connected by a tube to a vertical condenser. The flask is then heated gently so that the PCl_5 may react on the excess of red phosphorus; finally, it is distilled, and the product is obtained free from free phosphorus.—*Berichte*, xxxiv., p. 645.

NOTICES OF BOOKS.

Water Supply. Considered Principally from a Sanitary Standpoint. By WILLIAM P. MASON. Third Edition, Re-written. New York: John Wiley and Sons. London: Chapman and Hall, Lim. 1902. Pp.vii.-448. 8vo. Illustrated. Cloth.

THE author of this valuable work might have used the following lines by way of introduction:—

" Traverse the desert, and then ye can tell
What treasures exist in the cold deep well
Sink in despair on the red parch'd earth,
And then ye may reckon what water is worth,"

since it deals with the value of normal water, the insidious dangers of polluted water, the relations of disease to drinking waters, methods for the artificial purification of water, as by filter-beds on a large scale, rain, ice, and snow as sources of water, surface and deep-seated waters, and water statistics.

The opening chapter, which is short, contains some account of the magnitude of ancient water supplies, with especial reference to Rome; the second chapter considers the question of the wholesomeness of water, and cites striking instances of dangerous epidemics of cholera and typhoid disseminated by means of drinking-water. The different conditions in Hamburg and in Altona during the terrible outbreak of cholera in 1892 are clearly described and the circumstances leading to the prevalence of typhoid fever in certain localities are made known; on the whole, the author finds that it is not a simple or easy matter to define "good, pure, wholesome water." The artificial purification of water by mechanical filtration as carried on in England and in Germany and the American Filter System are detailed in Chapter III., the descriptions being facilitated by the aid of diagrams, plans, and photographic views. The author has studied systems of water supply in many parts of Europe; he describes in an interesting way the underground storage systems of Naples, and of Gibraltar, where he enjoyed unusual opportunities.

This third edition has been practically re-written, and the chapters in earlier editions on the chemical and bacteriological examination of water have been omitted, appearing independently in book-form. The sources of information are scrupulously acknowledged. The volume is embellished by handsome illustrations, and its utility is enhanced by a very full index. H. C. B.

The Principles of Inorganic Chemistry. By WILHELM OSTWALD. Translated with the Author's sanction by ALEXANDER FINDLAY, M.A., B.Sc., Ph.D. With 122 Figures in the Text. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1902. Pp. 785.

THIS translation of the "Grundlinien der Anorganischen Chemie" will doubtless contribute to a more widespread knowledge of the recent developments of general chemistry, and their importance in the study of the other branches of the science.

The work, which is divided into no fewer than forty-four chapters, begins with a discussion of general principles, the laws of conservation, the phenomena of combustion, &c.; it then deals seriatim, chapter after chapter, with all the known chemical elements, giving first a few general remarks on their characteristics, properties, appearance, &c.; then their compounds are dealt with, not only from the chemical, but from the physical point of view; this is more especially the case with regard to gases, their liquefaction and solidification.

The general intention of the author has been to make a book of pure chemistry; regard has been paid to the related sciences and arts, only in so far as chemical questions play a part in them; by this means the student will obtain a thorough "grounding" in chemistry, and will find it easier to apply his knowledge in later years.

The book is well printed and extensively indexed.

New York Agricultura Experiment Station, Geneva, N.Y.
Published by the Station.

WE have just received Nos. 207 to 211 inclusive of these Bulletins. The one having most chemical interest is No. 208, on "Stable Manure and Nitrogenous Chemical Fertilisers for Forcing Lettuce," by S. A. Beach and H. Hasselbring. In these experiments nitrogenous commercial fertilisers were compared with each other as to their effect on forcing lettuce, and the particular forms in which they were tested were dried blood, nitrate of soda, these two combined, and sulphate of ammonia.

The use of these fertilisers without stable manure resulted in a decided increase in yield over crops on corresponding untreated soil, but were inadequate in forcing the lettuce in a sufficiently short time to be profitable.

On clay loam with no stable manure a better yield was generally obtained with nitrate of soda than with either sulphate of ammonia or dried blood. On sandy soil dried blood generally gave superior results to those obtained with nitrate of soda or sulphate of ammonia. With sulphate of ammonia the results were very variable. The best crops were those obtained where the soil was fertilised with stable manure. Five per cent of this latter added to commercial fertilisers always showed a very great increase in yield; further increase in the manure, however, was not followed by a corresponding increase in the yield. The report contains a number of photographs and figures showing the size and yield of the lettuces obtained under the various conditions tried.

Bulletin No. 211 contains the Director's Report for 1901, and, as in former years, is made up chiefly of the results of investigations and experiments of a scientific or semi-scientific character; that is to say, it is the outcome of efforts made to study problems or conditions important to the practice of agriculture, and is not intended, for the most part, to give information of a common or general character.

Lehrbuch der Anorganischen Chemie. By Dr. H. ERDMANN. Third Edition. Braunschweig: Friedrich Viewig und Sohn. 1902.

THE third edition of this text-book of inorganic chemistry, the first edition of which was published some three years ago, has been enlarged and brought up-to-date. The practical uses and applications of the substances described, their therapeutic effects and importance in every-day life, receive considerable attention, and the book may be specially recommended to those members of various professions to whom some chemical knowledge is indispensable. The general arrangement and marginal headings make it easy to consult as a book of reference. The first part gives a review of chemical theory, Part II. deals with the non-metals, and Part III. with the metals; while an appendix is added on the periodic system and electro-chemistry. The book is well illustrated, and includes most useful tables of chemical and physical data, logarithms and anti-logarithms, as well as the ingenious spiral table of the periodic law devised by Erdmann and Koethner. It appears to be, for its size, one of the most exhaustive text-books extant, and is certain to be widely appreciated.

Chemisch-Analytisches Praktikum. By Dr. KARL ANTON HENNIGER. Braunschweig: Friedrich Viewig und Sohn. 1902.

THIS book provides a first course in practical chemistry and qualitative analysis for schools, and is specially suited to beginners. The opening chapters on the preparation and general properties of salts, the use of acids as solvents, and the treatment of insoluble bodies, deserve much praise. The rest of the book, giving the reactions of the more common acid-radicals and metals, and directions for the analysis of simple substances and mixtures, does not display marked originality of treatment; it is,

however, methodical and clear, and equations and explanatory comments are freely introduced, while the importance of constant recapitulation is emphasised—all features likely to commend themselves to class-teachers.

CORRESPONDENCE.

ATOMS AND ENERGIES.

To the Editor of the Chemical News.

SIR,—In reference to the notice in the last issue of the CHEMICAL NEWS of Mr. D. A. Murray's book on "Atoms and Energies," would you kindly allow me to point out that the views in that book for which novelty seems to be claimed—the views, namely, as to atoms being of certain sizes and shapes which determine their ways of combining, and as to energy being a distinct entity in two forms which together constitute the ether—seem, broadly speaking, to be identical with those I have long been putting forward.

It may be remembered that in the CHEMICAL NEWS of March 22, 1895 (vol. lxxi., p. 139) I showed how to deduce the shape of the atom both for metals and metalloids from the series in the Periodic System with the help of inactive elements.

In my books "Force as an Entity," "Argon and Newton," and "The Advance of Knowledge" I have given drawings of the shapes thus arrived at.

I notice that Mr. D. A. Murray's views show energy and the ether to be penetrable and infinitely divisible, while I have been endeavouring to show that energy and the ether are corpuscular in constitution, being made up of corpuscles of two kinds which differ in strength.

Corpuscles of the strong form are apparently Prof. J. J. Thomson's "corpuscles," Sir William Crookes's radiant matter, and Newton's "Agents in Nature able to make the particles of bodies stick together by very strong attractions" (*Opticks*, 3rd ed., p. 369). Corpuscles of the two kinds together give an ether composed of two fluids and apparently give also Dr. Larmor's "electrons."—I am, &c.,

W. SEDGWICK,
Lt.-Col. (late R.E.).

Elmcote, Godalming, June 4, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

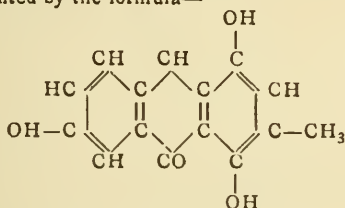
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiv., No. 19, May 12, 1902.

Lithium Silicide.—Henri Moissan.—When a mixture of pure amorphous or crystalline silicon is heated *in vacuo* with a metal such as sodium or potassium to the boiling-point of the metal, a very small quantity of the silicide is produced. The separation of this is, however, very difficult, and this reaction cannot be used as a means of preparation of the silicide. In the case of lithium, however, the author succeeds in preparing lithium silicide, Si_2Li_6 , by the above method. At the end of the reaction the excess of lithium is distilled off, and a very hygroscopic blue-violet mass remains in the crucible. The pure lithium silicide is in the form of dark indigo-blue brilliant crystals, which, when examined under the microscope, appear quite homogeneous. Their density is about 1.12, and the crystals are dissociable *in vacuo* above 600° , giving vapours of lithium and leaving amorphous silicon. An analysis of this substance shows it to have the formula Si_2Li_6 .

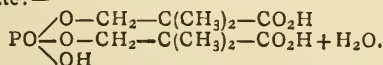
Conditions of Formation and Stability of the Hydrides and Nitrides of the Alkaline Earths.—Henri Gautier.—The absorption of hydrogen by the three alkaline earth metals begins at the same temperature for the alloys of cadmium, and this temperature is lowered when the proportion of the alkaline-earth metal contained in the alloy increases. Starting from the same alloys of cadmium with the three alkaline-earth metals, the author verifies the fact that the metals only combine with nitrogen at a much higher temperature than that at which they combine with hydrogen; the absorption of nitrogen scarcely starting at 600°, and the nitride formed being undecomposed at 1000°—a temperature at which the hydrides are very strongly dissociated.

Some Derivatives of Anthraquinone obtained during the Action of Sodium Dioxide on the Aloines and their Halogen Products.—E. Léger.—When sodium dioxide acts on barbaloine and isobarbaloine, the liquid takes a dark red colour. The body thus prepared presents the composition of a trioxymethylantraquinone. The author investigates the composition of this substance, and finds that the product of oxidation of the aloines can be represented by the formula—



The position of the substituted groups is not, however, certainly established.

A New Dimethylglutaric Acid.—E. E. Blaise.—In a preceding paper the author showed that the condensation of bromoisobutyric ether with trioxymethylene gives ethyl oxypivalate, boiling at 85–87°. This substance reacts on phosphorus pentabromide, and gives ethyl bromopivalate, boiling at 83–84° under 20 m.m. pressure. The yield of bromo ether is only about 35 per cent—a fact which shows that the phosphorus oxybromide which is formed itself reacts on the ethyl oxypivalate, and, in addition to the bromo-ether, an oily acid liquid is produced which can be saponified by potassium and gives the dioxy-pivalic phosphate:—



This body crystallises very well from acetic ether and becomes anhydrous at 147°. It behaves as a tri-acid towards phthalein, giving well-crystallised salts, and it presents an extraordinary resistance to saponification.

Synthesis of Menthone.—Georges Leser.—Menthoximic acid was prepared according to Ad. von Baeyer and Manasse's method, by treating the ketone with amyl nitrite and hydrochloric acid. After crystallisation from aqueous alcohol the fusion-point is found to be 98–99°, and the analysis shows the formula to be $\text{C}_{10}\text{H}_{19}\text{O}_3\text{N}$. The author is continuing his research on this synthetic menthene.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxv., No. 24.

Remarks on the Colloids.—G. Wyruboff.—Not suitable for abstraction.

Contribution to the Study of the Luteo-cobaltic Salts.—T. Klobb.—The author shows that most of the luteo-cobaltic salts can be prepared directly, and he also describes the new salts obtained in the course of his research. The first is the luteo-cobaltic chloride, $(\text{Co}.6\text{NH}_3)\text{Cl}_3$. Thirty grms. $\text{CoCl}_2.6\text{H}_2\text{O}$ and 60 grms.

NH_4Cl are dissolved in 150 c.c. of water; this, while warm, is poured into 250 c.c. of ammonia cooled to 0°, the flask being kept in ice, while a current of air is passed so long as the blackish brown colour increases; 60 grms. of PbO_2 are then added, and the whole heated to boiling on the water-bath with constant stirring; a lively effervescence takes place. After filtration, the residue is washed with 50 c.c. of boiling water and left to crystallise. The salt is collected after twenty-four hours, and purified by re-crystallisation at 70°. The nitrate is prepared in a somewhat similar manner from the nitrate of cobalt. The author also describes the preparation of other salts, such as the neutral and acid sulphates, the chloride-chromate, the neutral, acid, and double seleniates, the acetate and succinate, &c. In all these preparations of luteo-cobaltic salts, if the sal-ammoniac is suppressed, leaving the other quantities constant, roseo-cobaltic salts are obtained almost exclusively; with the sulphate alone, a little hexammoniated salt is formed at the same time.

Action of Dilute Mineral Acids on Amino-dimethylacrylate of Ethyl.—L. Bouveault and A. Wahl.—Not suitable for abstraction.

Action of Nitric Acid on Toluene-*o*-nitro-*p*-sulphamide-1.2.4, and Nitration of *p*-Sulphochloride of Toluene.—F. Reverdin and P. Crépieux.—The authors added 10 grms. of *p*-sulphochloride of toluene to a mixture of 20 grms. of fuming nitric acid ($D=1.518$) and 30 grms. of concentrated sulphuric acid, keeping the temperature low. After standing for twenty-four hours, two layers of liquid were observed; one an oil, the other an acid liquid. The oil, treated in the cold with carbonate of soda till neutral, gave a yellowish product which could not be crystallised, but which fused at 36°. This body was identified as the *p*-sulphochloride of *o*-nitrotoluene, hitherto described as an oil; by the action of warm aqueous ammonia it gave toluene-*o*-nitro-*p*-sulphamide, $\text{C}_6\text{H}_3.\text{CH}_3.\text{NO}_2.\text{SO}_2\text{NH}_2$, fusible at 144°.

Some Derivatives of *p*-Sulphochloride of Toluene and of the *o*-nitro-*p*-sulphochloride of Toluene.—F. Reverdin and P. Crépieux.—The authors describe the preparation and properties of a number of phenol and ammoniac derivatives of *p*-sulphochloride of toluene and *o*-nitro *p*-sulphochloride of toluene, with their analyses and formulæ.

Use of Salicylate of Sodium for the Estimation of Mixtures of Terpenic Alcohols and their Ethers.—G. Darzens and P. Armingeat.—Already inserted in full.

MISCELLANEOUS.

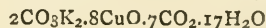
Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., The Duke of Northumberland, President, in the Chair. Mr. J. Christie, Mr. F. K. McClean, and Sir John Denison Pender were elected members.

Solubility of Salts. The Chromates of Sodium.—F. Mylius and R. Funk.—Soda and chromic anhydride combine, giving the following series of salts, of which the solubility at 18° has been determined; the acid and basic extremes are also included:—

	Density	Molecules of of the the salt per saturated 100 mols. solutions. of water.
Chromic anhydride, CrO_3	1.705	29.91
Tetrachromate, $\text{Na}_2\text{O}.4\text{CrO}_3+4\text{H}_2\text{O}$..	1.926	11.27
Trichromate, $\text{Na}_2\text{O}.3\text{CrO}_3+\text{H}_2\text{O}$..	2.059	20.56
Dichromate, $\text{Cr}_2\text{O}_7\text{Na}_2+10\text{H}_2\text{O}$..	1.745	12.16
Neutral chromate, $\text{CrO}_4\text{Na}_2+10\text{H}_2\text{O}$..	1.432	7.43
Hemi-chromate, $2\text{Na}_2\text{O}. \text{CrO}_3+13\text{H}_2\text{O}$..	1.426	4.81
Soda, $\text{NaOH}+\text{H}_2\text{O}$	1.539	37.80
Tetrachromate of sodium, $\text{Na}_2\text{O}.4\text{CrO}_3+4\text{H}_2\text{O}$, is in thin, deliquescent, reddish flakes, partially fusible at 40–50°		

with the separation of CrO_3 , otherwise stable on contact with water, contrary to the corresponding salts of potassium and ammonium. At the other end of the series the basic chromate, $2\text{Na}_2\text{O} \cdot \text{CrO}_3 + 13\text{H}_2\text{O}$, is found in large pale yellow flakes, very soluble, and fusible at about 50° . The neutral chromate occurs with $10\text{H}_2\text{O}$, with $4\text{H}_2\text{O}$, and also anhydrous. The second of these hydrates has no analogue in the series of sulphates of sodium; it is formed between 20° and 65° .—*Berichte*, vol. xxxiii., p. 3686.

The Alkalino-cupric Carbonates.—M. Gröger.—A concentrated solution of bicarbonate of potassium saturated with carbonic acid, being treated progressively in the cold with a solution of sulphate of copper, gives a deep blue liquor, which, after several days, deposits silky needles of a greenish-blue colour, decomposed by distilled water, giving a basic carbonate of copper and bicarbonate of potassium. These needles have the composition—



or— $4\text{CO}_3\text{KH} \cdot 8\text{CuO} \cdot 5\text{CO}_2 \cdot 15\text{H}_2\text{O}$.

Déville (*Ann. Chim. Phys.*, Series 3, vol. xxix., p. 102) has described a carbonate of the composition $\text{CO}_3\text{K}_2 \cdot 5\text{CuO} \cdot 4\text{CO}_2 \cdot 10\text{H}_2\text{O}$. This salt was obtained in the presence of CO_3K_2 , and might be mixed with a little basic carbonate of copper; it is probably identical with that of the author. Things happen differently in the case of bicarbonate of soda; we only obtain a definite product in the presence of the neutral carbonate. If we dissolve 20 grms. of CO_3Na_2 and 50 grms. of CO_3NaH in 700 c.c. of water, and add 8 grms. of $\text{SO}_4\text{Cu} + 5\text{H}_2\text{O}$ dissolved in 20 c.c. of water, we find that the filtered liquid deposits, in one night, pale blue tufts of a neutral sodio-cupric carbonate with the very simple formula $\text{CO}_3\text{Na}_2 \cdot \text{CO}_3\text{Cu} \cdot 3\text{H}_2\text{O}$. The deposit of this salt, like that of the preceding ones, is accelerated in the presence of a solid alkaline bicarbonate, and the crystals are then less needle-like.—*Berichte*, vol. xxxix., p. 429.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

River Water.—I should be much obliged if any of your readers could give me any particulars of analyses of river water from the Argentine Republic, Chili, or any of the South American States.—ERNEST A. LEWIS.

Iodine and Starch Test-paper.—Will you be good enough to inform me if it is possible by any method or chemical to render permanent the colour produced by the presence of iodine on chemical test-paper composed of starch-paste. When iodine is present, this paper assumes a blue colour, or blue marks are produced, which fade or disappear in the course of a day or two, but which I desire to make permanent.—CHEMICAL.

MEETINGS FOR THE WEEK.

FRIDAY, 13th.—Royal Institution, 9. "The Progress of Electric Space Telegraphy," by G. Marconi.
Physical, 3.30. (At the National Physical Laboratory, Bushy House, Teddington).

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THE CHEMICAL NEWS.

VOL. LXXXV., No. 2220.

COEFFICIENTS OF THE CUBICAL EXPANSION OF ICE, HYDRATED SALTS, SOLID CARBONIC ACID, AND OTHER SUBSTANCES AT LOW TEMPERATURES.*

By JAMES DEWAR, M.A., D.Sc., LL.D.,
Jacksonian Professor, Cambridge University, and
Fullerian, Royal Institution, London.

THE apparent specific gravities of boiling liquid oxygen which resulted from weighing in the liquid a series of metals and other substances were given in a lecture entitled "New Researches on Liquid Air," printed in the Royal Institution *Proceedings* for 1896. For instance, silver, calc-spar, rock crystal, and iodide of silver gave the respective apparent densities 1.1278, 1.1352, 1.1316, and 1.1372. On correcting the weight of liquid displaced by each substance for contraction to -182.6° —by calculating a Pizeau mean coefficient of expansion for the range of temperature employed, on the assumption that the parabolic formula might be legitimately extended to low temperatures—it was found that the real density of liquid oxygen so deduced for all the bodies used was, as a mean, 1.137.

The determination of the densities of substances at the temperature of the boiling-point of oxygen—and hence of their mean coefficients of expansion between that temperature and ordinary temperatures—opens out a very large field of investigation, from which, if a sufficiently large number of observations were available, valuable deductions might be drawn. On account, however, of the expense and trouble of producing quantities of liquid oxygen, its use for this purpose is not likely to become general, although, when available, it is the easiest body to use in conducting such experiments, especially when the vacuum vessel containing it is immersed in a larger vessel containing the same fluid or well evaporated air. The ease with which liquid air can now be obtained in many laboratories suggests that its application to work of this kind would in some cases be a convenience, and the present investigation was undertaken with the desire of ascertaining what accuracy could be attained, and how the method could be applied to inorganic or organic substances which occur in the form of fine crystals. The use of a mixture of varying composition and density like liquid air necessitates a determination of its density with accuracy and rapidity before and during the course of the experiments. For this purpose, in the experiments about to be detailed, the liquid air that had been allowed to evaporate for twenty-four hours in advance was used in large silver-coated vacuum vessels of some 3 litres capacity. In order to ascertain the density of the liquid, a polished silver ball, which had been weighed once for all in liquid oxygen, was weighed in the sample of liquid air, and from the relative weights thus found the density of the liquid air could be approximately determined, assuming that of liquid oxygen to be 1.137.† To prevent any disturbing ebullition in the liquid-air flask in which the weighings took place, and to reduce the rate of its evaporation to a minimum during the course of an experiment, the substance to be used was previously cooled in a supplementary vessel containing liquid air, and then transferred to the large flask. To avoid as far as possible the formation of cracks in the bodies during the process of immersion in the liquid air, it was found advisable to cool

them slowly in the air of the vacuum flask first, and then to lower them into the liquid. In this way, with proper care and attention, results were obtained comparable in accuracy with the density taken in liquid oxygen. Substances like solid carbonic acid and ice were weighed in the cool, gaseous air of the vacuum vessel, and their weights subsequently corrected for buoyancy. The temperature of the densest and lightest samples of liquid air were ascertained by the hydrogen thermometer, and that of the others deduced by graphic interpolation. As the entire range of temperature through which the bodies were cooled amounted to about 200° , a degree or two up or down has no real influence on the results; the extreme range of temperature in the air samples was from 83.8° to 86.1° Abs.

When the body to be examined was a salt, it was employed in the form of a compressed block. One experiment was, however, made in a section of a large crystal of chrome-alum. The salt, previously reduced to a fine powder, was moistened with water and compressed in a cylindrical steel mould under great hydraulic pressure. During compression the saturated salt solution drained away, and finally a cylindrical block of some 50 grms. of the salt was obtained free from porosity and hard enough to allow its surface to be polished. In this form salts and other materials similarly treated are especially adapted for accurate specific gravity determinations. After such treatment it was found that all the mechanically attached water was got rid of in the case of hydrated salts, and also in such as did not combine with water. In order to get cylindrical blocks of the salts showing no porosity, the presence of water, or rather the saturated salt solution, was found to be essential during the application of pressure. In the same way it was found to be an advantage in compressing such a substance as solid carbonic acid, to moisten it with a fluid like ether before applying the hydraulic pressure.

Recalling the work of Playfair and Joule ("Researches on Atomic Volume and Specific Gravity," *Chem. Soc. Journ.*, vol. i., 121), which originated in a suggestion of Dalton's that the volume of a hydrated salt in solution was simply the volume of the water of crystallisation, ice and some hydrated salts were selected, as well as some other bodies whose coefficients of expansion they had determined. Substances of special interest were included in the list, like mercury, sulphur, iodine, and solid carbonic acid, the latter being particularly important as an example of a solidified gas.

In the further conduct of an experiment the observations made on a substance were three, namely:—(A) the weight in grammes of the substance and suspending platinum wire, either in air of about 17° C. temperature or in the gaseous air in the flask containing the liquid air; (B) the weight in grammes of the body and wire when immersed in the liquid air; and (C) the weight in grammes of the suspending platinum wire in ordinary (17°) air. This wire was bent into the form of a small cage, to hold the compressed cylinder or portion of the substance to be examined. (C) was measured once for all for each cage, and in the different cases varied from about 0.2 to 0.3 grms. The relative portion of wire not immersed in liquid air was so small that no appreciable error will be made in (B) by considering that the whole of the wire was immersed. Further, no allowance is made for the (17°) air displaced by the weights themselves. The observed weights A, B, C are therefore connected with the weights and specific gravities of the substances concerned by the very approximate relations.

$$A = W + w - \frac{W}{S} d - \frac{w}{s} d,$$

$$B = W + w - \frac{W}{S} D - \frac{w}{s} D,$$

$$C = w - \frac{w}{s} d,$$

* A Paper read before the Royal Society, May 1, 1902.

† As the correction due to the contraction of the silver ball between the temperature of boiling oxygen and that of the air sample is small, it may be neglected.

where W = true weight of substance examined.

w = true weight of platinum wire.

S = specific gravity of substance required.

D = specific gravity of liquid air, when B was observed.

d = specific gravity of gaseous air, when A was observed.

s = specific gravity of platinum.

From these relations we derive—

$$S = \frac{A - C - B \frac{d}{D} + C \frac{d}{D} \frac{s - D}{s - d}}{A - B - C \frac{D - d}{s - d}} D,$$

instead of which we may write—

$$S = \frac{A - C}{A - B} D \times \text{correcting factor.}$$

The correcting factor is—

$$\frac{1 - \frac{B - C \frac{s - D}{s - d}}{A - C}}{1 - \frac{D - d}{s - d} \frac{C}{A - B}},$$

which in the present circumstances differs from unity only by a few units on 10 000.

In the subjoined Table I. are given the values of $A - C$, $A - B$, and D for each observation.

In the case of substances of less density than liquid air, a polished copper ball weighing 38 grms. was used as a sinker. The details of the ice experiments, three in number, are given in Table II.

Two experiments were made on compressed cylinders of solid carbonic acid. In the first of these the carbonic acid was compressed dry, in the second after a few drops of ether were added. The specific gravities of solid mercury, iodine, and sulphur were also determined in liquid air. The iodine was in the form of a compressed cylinder, but the sulphur was a piece of a crystalline mass of native origin.

The specific gravity of the actual portion of the substance weighed in the liquid air was, with one or two exceptions, determined also at the temperature of the laboratory, about 17°C . From the two sets of observations the value of the mean coefficient of cubical expansion between 17°C ., and the temperature of liquid air, was calculated.

In calculating coefficients of expansion, various forms may be given to the formula employed, and correspondingly different results may be obtained from the same set of observations. For short ranges of temperature these results are practically identical, but this no longer holds for a range of temperature such as we have in these experiments. All that is possible in the present instance is to adopt a linear formula. The usual formula is $v_T = v_0 (1 + \alpha T)$, where the value v_0 at 0°C . becomes v_T at $T^\circ \text{C}$. when α is the coefficient of expansion. If we use densities (d) instead of volumes (v) this formula becomes—

$$d_0 = d_T (1 + \alpha T), \quad \text{or} \quad \alpha = \frac{d_0 - d_T}{T d_T}; \quad \alpha = 0.000538.$$

Another formula, when T and T' are the temperatures dealt with, is—

$$d_T = d_{T'} \{1 + \alpha (T' - T)\}, \quad \text{or} \quad \alpha = \frac{d_T - d_{T'}}{(T' - T) d_{T'}}; \quad \alpha = 0.000595.$$

Again—

$$d_{T'} = d_T \{1 - \alpha (T' - T)\}, \quad \text{or} \quad \alpha = \frac{d_T - d_{T'}}{(T' - T) d_T}; \quad \alpha = 0.000558.$$

Also we may choose a mean formula—

$$\alpha = \frac{d_T - d_{T'}}{(T' - T) \frac{d_T + d_{T'}}{2}}; \quad \alpha = 0.000576.$$

The differences in the results of applying these formulæ are shown in the numerical values attached to each, which are calculated from the first experiment on solid carbonic acid in Table III., coupled with the specific gravity 1.53 of the solid at -78°C .

Perhaps as a matter of general convenience, the first of these formulæ is the best; however, the second was chosen to conform with the old work of Playfair and Joule, and it is the results of this formula which appear in the table.

The temperature range is taken from about -186°C . to 17°C ., unless otherwise stated.

Ice.—In determining the density at the temperature of liquid air of pieces of clear ice cut from large blocks, both the silver and copper balls already referred to were used as indicated. The true weight *in vacuo* of the silver ball was 132.2855 grms., and that of the copper ball was 38.0802 grms. The observations and results are given in Table II. The mean of the three densities at -188.7°C . is 0.92999.

Recently Vincent (*Roy. Soc. Proc.*, 1901) has re-determined the density of artificial ice at the freezing-point, and also its coefficient of expansion. He finds the density to be 0.916, or from his tabulated results 0.91599. Playfair and Joule find the mean of the densities given by eight observers previous to them, to be 0.919, and they themselves get 0.9184; Bunsen found it to be 0.9167. If we take this most recent determination, namely, 0.91599 at 0° , and 0.92999 at -188.7° , and use the formula—

$$d_0 = d_T (1 + \alpha T)$$

we get $\alpha = 0.00008099$.

Vincent refers to "only one" estimate for natural ice, namely, 0.0001125, adding that "the mean of three available results for artificial ice is 0.000160"; finally, he gives the mean of four determinations of his own, namely, 0.000152. Apparently then, we may take 0.0001551 as the mean coefficient of expansion of ice between 0° and (say) -20°C . Thus the mean coefficient of expansion between 0° and -188°C . is about half of that between 0° and -20°C . The mean coefficient of expansion of water in passing from 4° to -10° is -0.000362 , and from 4° to 40°C . it is 0.0002155. Hence the mean coefficient of expansion of ice between 0° and -188°C ., is about one-fourth of that of water between 0° and -10°C ., and half of that between 4° and 100°C .

If we had the densities of ice at still lower temperatures, the values of the coefficient of expansion thence determined would, we have every reason to believe, be less than what we have found. We shall therefore not be overstraining the argument if we use the value just found to determine an upper limit to the density of ice at the absolute zero. The result is 0.9368, corresponding to a specific volume 1.0675. Now the lowest density of water, namely, at the boiling-point, is 0.9586 (corresponding to specific volume 1.0432), so that ice can never be cooled low enough to reduce its volume to that of the liquid taken at any temperature under one atmosphere pressure. In other words, ice molecules can never be so closely packed by thermal contraction as the water molecules are in the liquid condition, or the volume of ice at the absolute zero is not the minimum volume of the water molecules. It has been observed by Professor Poynting ("Change of State, Solid, Liquid," *Phil. Mag.*, 1881) that if we suppose water could be cooled without freezing, then taking Brunner's coefficient for ice, and Hallstrom's formula for the volume of water at temperatures below 4°C ., it follows that ice and water would have the same specific volume at some temperature between -120° and -130° ; applying the ordinary thermodynamic relation, then no change of state between ice and water could be brought about below this temperature. On the other hand, Clausius ("Mechanical Theory of Heat," 1879, p. 172) has shown that the latent heat of fusion of ice must be lowered with the temperature of fusion some 0.603 of a unit per degree. If such a decrement is

assumed to be constant, then about -130° the latent heat of fluidity would vanish.* Baynes discusses the same subject ("Lessons on Thermodynamics," 1878, p. 169), and arrives at the conclusion that at a temperature of -122.8° C. and under a pressure of 16,632 atmospheres there is no distinction between the solid and liquid forms of water. At temperatures below this limit no amount of pressure would transform ice into water. We are thus relieved from a difficulty that would follow but for this demonstration of Clausius, namely, that the application of enormous pressures to ice, even at temperatures below that of liquid hydrogen, might cause the transformation of ice into water.

Carbonic Acid.—Two experiments were made with this substance, the masses in each case being about 20 grms. These were compressed cylinders; the former was compressed dry, while the latter was slightly moistened with ether. The data and results are given in Table III.

The density of solid carbonic acid at its boiling-point was formally given as 1.5 (see *Proc. Roy. Inst.*, 1878, "The Liquefaction of Gases"), but the mean of my results at the time came to 1.53. Recently the same value has been found by Behn. Taking this value and 1.6267, the mean of the above results at -188.8° C., and using the formula $d_T = d_T' \{1 + \alpha (T' - T)\}$ we get $\alpha = 0.0005704$.

This is a very large coefficient of expansion, being greater than that of any substance recorded in Table I., and comparable with that of sulphur between 80° and 100° , which, according to Kopp, is 0.00062. The coefficient of liquid carbonic acid at its melting-point taken from the recent observations of Behn (*Chem. Journ.*, 1901) is 0.002989, so that the rate of expansion of the liquid at its smallest value is very nearly five times that of the solid.

Solid Mercury.—One experiment was made with solid mercury, of which the details are given in Table I.

Mallet determined with great accuracy the density of solid mercury at -38.85° , his result being 14.193; coupling this with the density found for the liquid-air temperature, we find the value of the coefficient of expansion between the melting-point and -189° C. is 0.0000887. For fluid mercury above 0° C. the mean value is about 0.000182, so that in the solid state this coefficient is about half of that in the fluid state.

(To be continued).

ON THE PREPARATION OF TANTALUM BY THE ELECTRIC FURNACE, AND ON ITS PROPERTIES.

By HENRI MOISSAN.

In a previous paper it has been shown that niobite reduced to powder and mixed with sugar charcoal, gives, in the electric furnace, a button rich in niobium and in tantalum. The metallic mass, treated with hydrofluoric acid containing a little nitric acid, then by fluoride of potassium, gave a mixture of fluotantalate and fluoxyniobate of potassium. On applying Marignac's method of separation to these salts we were able to prepare about 4 kilograms of fluoxyniobate and fluotantalate of potassium.

The mixture of these two salts was exhausted six times with boiling water. The fluotantalate remaining, after having been washed with distilled water, was decomposed with its own weight of sulphuric acid in a platinum crucible. The white precipitate, carefully washed with warm water, was calcined. The tantalic acid still contained 0.32 per cent of sulphur in the form of sulphuric acid in combination, after washing and calcination. Ten

per cent of pure carbonate of ammonium were mixed with this tantalic acid and calcined. This operation was repeated twice.

After having made sure of the purity of the tantalic acid, by means of its density and by its molecular weight, we attempted to reduce it by means of carbon at the temperature of the electric furnace.

We recalled the fact that Berzelius by heating the fluotantalate of potassium with potassium obtained a greyish powder which did not conduct electricity, and had a density of 10.08. Henri Rose, by decomposing the fluotantalate of sodium by metallic sodium, obtained a black powder with a density of 10.78, and which was, further, a good conductor of electricity.

Children, by the electrolysis of tantalic acid with an intense current, obtained a tantalum with a reddish-yellow colour and which was very brittle.

Finally, Marignac, by decomposing a fluotantalate with aluminium, prepared and described a crystallised alloy of tantalum and aluminium.

Tantalic acid has been regarded up to the present as being infusible and irreducible by carbon. We have treated this tantalic acid with a quantity of sugar carbon corresponding to the reaction $Ta_2O_5 + 5C = 2Ta + 5CO$.

To obtain a button containing only a small amount of carbon it is advisable to increase the proportion of tantalic acid by one-tenth.

The mixture was agglomerated by pressure into the form of small cylinders, which were heated in a Perrot furnace in a brasque of sugar charcoal. After this calcination, which gives a certain consistency to the mixture, the cylinders are arranged in a graphite crucible, which is heated in the electric furnace. The cylinders may also be placed in a graphite boat in the centre of a tube formed of the same substance. In both cases the temperature used should be very high if we wish to melt the resulting ingot of tantalum. If this is not done, though the reduction is properly effected, the cylinders, while fritting a little, still keep their shape approximately, and have under a lens a cavernous metallic appearance, and are covered with a yellow or orange layer. After heating for five minutes with a current of 800 ampères and 60 volts only a fritted mass is obtained; it is necessary to heat for ten minutes to effect the fusion of the tantalum.

Properties of Tantalum.

This tantalum when it is sufficiently heated occurs in the form of a brilliant metallic mass with a crystalline fracture. Certain preparations have given us an ingot containing no more than 0.5 per cent of carbon, but in this case more than half the tantalum was volatilised during the operation. This sample, containing such a small quantity of carbon, scratches glass and rock-crystal with ease; it is infusible before the oxyhydrogen blow-pipe, which transforms it rapidly into tantalic acid. It can be fused in the electric furnace, but only with a very powerful arc. Its density has been found to be 12.79, while the density of the tantalum prepared by Berzelius was 10.08, and that of Rose's tantalum 10.78.

Finely powdered tantalum takes fire when gently heated in fluorine, and gives off abundant vapours which, on condensation on a cold body, form a fluoride.

In a current of chlorine the attack of tantalum commences slowly at 150° . It increases at about 200° , and finally at 250° the combination takes place with incandescence; a chloride of tantalum is sublimed in the form of long orange-yellow needles. This chloride is easily fusible, and volatilises with decomposition in an atmosphere of chlorine. Bromine can be distilled over powdered tantalum without producing any reaction, but at a dull red heat it commences to give a yellow sublimate, and at the temperature of the softening of glass the reaction becomes complete with the disengagement of a large quantity of heat.

The vapour of iodine does not react on tantalum, even at a temperature of 600° .

* In my paper "On the Lowering of the Freezing-point of Water by Pressure" (*Roy. Soc. Proc.*, 1880), it was proved that up to 700 atmospheres the rate of fall was constant and equal to the theoretical value within the range of pressure if the difference between the specific volumes of ice and water remain constant; thence the latent heat of fusion must diminish just as Clausius had predicted.

If we place some tantalum in a current of dry oxygen it is necessary to raise it to a temperature of 600° (taken with a thermo-electric couple) before it takes fire, when it continues to burn with lively incandescence.

At a temperature of 700° sulphur, selenium, and tellurium do not react. When heated in a current of nitrogen at 1200° tantalum only increases very slightly in weight, and is not transformed into a nitride. Phosphorus and arsenic may be distilled over tantalum at the temperature of the softening of glass without producing any reaction. The same is the case with antimony.

An ingot of tantalum containing only 0.6 per cent of carbon did not combine with sodium, potassium, or zinc in fusion; when heated with iron in the electric furnace a small portion entered into combination, but the ingot did not show any homogeneity.

Hydrochloric acid gas attacks tantalum, giving a white sublimate, which becomes darker in colour as the temperature rises; at the same time hydrogen is given off. Water vapour and sulphuretted hydrogen do not react on tantalum at a temperature of 600° , or if any reaction does occur it is entirely superficial.

Ammonia-gas is decomposed at a dull red heat by powdered tantalum, of which the colour deepens without any change of weight. Sulphurous acid gas is reduced by tantalum with incandescence towards 500° , producing an abundant deposit of sulphur and an oxide of tantalum. At the same temperature nitrous and nitric oxides react with lively incandescence. Phosphoric anhydride is easily reduced above a red heat, giving off abundant fumes of phosphorus, but without incandescence.

Powdered tantalum gently heated with iodic anhydride becomes incandescent, and gives off abundant vapours of iodine. Arsenic acid is reduced by tantalum at above a red heat.

The compounds rich in oxygen, such as binioxide of manganese, are reduced by tantalum with incandescence.

Protoxide and binioxide of lead gently heated with powdered tantalum become incandescent, and leave a residue consisting of a black sponge containing small globules of melted lead. The protochloride and bichloride of mercury are easily reduced when heated, and give a sublimate of metallic mercury.

Fused potash is attacked by tantalum; it gives off hydrogen, and forms an alkaline salt. Heated chlorate of potash does not react on tantalum, even at its temperature of decomposition. We have already shown that the same was not the case with niobium. This is therefore one of the reactions which differentiates these two simple bodies.

The attack of tantalum by nitrate of potassium in fusion also proceeds more slowly than with niobium; there is no incandescence, and peroxide of nitrogen is given off.

Acids alone are without action on tantalum, with this exception—that boiling concentrated sulphuric acid attacks it very slowly, taking a brown colour. Aqua regia is without action, but in the same manner as with silicon and niobium, tantalum is easily attacked by a mixture of nitric and hydrofluoric acids.

These different reactions thus establish the fact that tantalum possesses very particular reducing powers, which cause it to resemble the metalloids rather than the metals.

Its reactions are similar to those of niobium. This parallelism is very pronounced, and the principal difference between these two simple bodies is that niobium is a more energetic reducing agent than tantalum.

Analysis.

The estimation of the carbon was made by combustion. A weighed quantity of the metal reduced to powder was heated in a boat in a current of oxygen. The whole of the carbon is transformed into carbonic acid, which is collected and weighed. From the increase in the weight of the boat we can calculate the amount of tannic acid formed and the amount of tantalum originally present.

Care must be taken in this analysis to make quite

certain that the tantalum has been completely transformed into tannic acid.

By this means we have found the following figures, taking 183 as the atomic weight of tantalum:—

	I.	II.	III.	IV.	V.
Combined carbon ..	2.5	1.8	1.1	0.66	0.5
Tantalum	96.7	97.35	—	—	—

—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 10.

THE ELECTROLYTIC SEPARATION OF MERCURY FROM COPPER.*

By C. ROSCOE SPARE and EDGAR F. SMITH.

At intervals, since the electrolytic separation of mercury from copper was first announced, statements have appeared that the separation was unsatisfactory. The first objection was to the length of time consumed, but it was soon observed in this laboratory that this factor was very materially reduced upon heating the electrolyte to 65° C. Then it was said that the separation was only applicable and satisfactory when the quantity of copper was not too large, as compared with the amount of mercury in the solution. Proper replies were made to these restrictions upon the method, but recently another chemist, in the person of Emil Goecke, published in his inaugural thesis "Ueber den Genauigkeitsgrad elektro-analytischer Arbeitsmethoden, &c.," that he not only required from sixteen to twenty-four hours to effect the separation, but in only three instances did he find the mercury free from copper. It is not the purpose of the writers to question Goecke's ability to conduct electrolytic work, or analytical work of any kind for that matter, but they feel that it is only fair to lay additional actual experience before the reader, leaving time and further trials to determine finally who is right. In this laboratory the method in question has been so frequently carried out with success that it seemed almost useless to repeat; but the following trials were undertaken, and the results are presented in the order in which they were obtained (see Table I.). The details are sufficiently indicated in the tables.

The deposit of mercury was, in each case, tested most carefully for copper, but the latter was never found. Why Goecke encountered the opposite experience we are not prepared to say. The only reagent used for washing was cold distilled water. The source of the electric energy was storage cells. The time factor here, as in numerous other experiments, is much reduced. From the abundance of evidence here presented on this topic and in former communications, we are disposed to leave the controversy to those who delight in such occupation. We submit facts; they alone settle difficulties.

Goecke emphasises the statement that carbon is present in metals deposited by the current from potassium cyanide solutions, "jedoch in so minimalen Mengen, dass dieselben für die Praxis kaum in Betracht kommen." Indeed, in but a single instance, did it attain to 0.1 per cent, so that another writer has said "aber in so minimaler Menge, dass die Versuchsfehler der Bestimmungsmethoden kaum überschritten wurden." And we are disposed to add that in all probability a more thorough washing of the precipitated mercury would have removed the last traces of alkaline cyanide, and the test for carbon would have resulted negatively.

One of the chief purposes of Goecke seems to have been the study of the impurities contained in metals precipitated on the cathode. He points to the occurrence of carbon in the iron deposited from a citrate solution. This fact was commented upon by the person who first precipitated iron from that electrolyte. It is an old story, and before long we shall very probably hear from Dr. E. F.

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xxiii., No. 8.

TABLE I.
In the approximate proportion of 1 Hg : 1 Cu.

Mercury. Grm.	Copper. Grm.	KCN. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature. °C.	Time. Hours.	Mercury found. Grm.
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = 0.03 A	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.7 \text{ V} \end{array} \right.$	65°	3 $\frac{3}{4}$	0.1211
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.05 \text{ A} \\ 0.03 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.9 \text{ V} \end{array} \right.$	60°	2 $\frac{1}{2}$	0.1208
0.1211	0.1520	2.5	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.015 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	63°	3 $\frac{3}{4}$	0.1211
1 Hg : 2 $\frac{1}{2}$ Cu.								
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.015 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	3 $\frac{1}{2}$	0.1202
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.02 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	3 $\frac{1}{2}$	0.1205
0.1211	0.3040	3.5	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.02 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	4	0.1210
1 Hg : 6 $\frac{1}{2}$ Cu.								
0.0453	0.3040	3.5	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.012 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.1 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	2 $\frac{1}{2}$	0.0453
0.0453	0.3040	3.5	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.02 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	3	0.0455
0.0453	0.3040	3.0	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.1 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	4 $\frac{1}{2}$	0.0449
1 Hg : 11 Cu.								
0.0453	0.5115	6.0	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.015 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	2 $\frac{3}{4}$	0.0453
0.0453	0.5115	7.5	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.015 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.1 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	3 $\frac{1}{2}$	0.0447
0.0453	0.5115	5.5	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	2 $\frac{1}{2}$	0.0454
3 Hg : 1 Cu.								
0.1211	0.0483	2.5	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.022 \text{ A} \\ 0.02 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.5 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	2 $\frac{3}{4}$	0.1210
0.1211	0.0483	2.3	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.5 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	4 $\frac{1}{4}$	0.1213
0.1211	0.0483	2.0	125	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.06 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.6 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	3	0.1205

TABLE II.

Mercury. Grm.	Copper. Grm.	Cadmium. Grm.	KCN. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature. °C.	Time. Hours.	Mercury found. Grm.
0.1211	0.1207	0.1410	4.0	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.04 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.4 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	3 $\frac{1}{4}$	0.1204
0.1211	0.1207	0.1410	3.5	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.04 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.2 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	3 $\frac{1}{2}$	0.1211
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.02 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.4 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	65°	4 $\frac{3}{4}$	0.1207
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.3 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	4 $\frac{1}{2}$	0.1203
0.1211	0.1207	0.1410	3.0	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.04 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.4 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	4	0.1208

TABLE III.

Mercury. Grm.	Copper. Grm.	Cadmium. Grm.	Zinc. Grm.	KCN. Grms.	Dilution. C.c.	Current.	Voltage.	Temperature. °C.	Time. Hours.	Mercury found. Grm.
0.1211	0.1207	0.1410	0.1000	9.0	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.02 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.4 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	5	0.1206
0.1211	0.1207	0.1410	0.1000	5.0	135	N.D. ₁₂₅ = $\left. \begin{array}{l} 0.03 \text{ A} \\ 0.01 \text{ A} \end{array} \right\}$	$\left\{ \begin{array}{l} 1.5 \text{ V} \\ 1.5 \text{ V} \end{array} \right.$	60°	3 $\frac{1}{4}$	0.1207

* Maximum and minimum currents.

Kern on this subject. He has executed a series of experiments showing upon what this co-precipitation of carbon is due and how it may be avoided. In time, too, we hope to speak of the occurrence of phosphorus in metals deposited from solutions of phosphates. Goecke records it as an ever-present impurity in the metals deposited from such electrolytes.

But to return to the electro-deposition of mercury. The literature relating to this reveals the fact that very little experimentation in this way has been done with mercury in the presence of three or four other metals. Indeed, this is a direction in which investigation could be profitably conducted. We submit results obtained by us in following this thought (see Tables II. and III.).

ANALYSIS OF THE VOLCANIC DUST
FROM THE RECENT ERUPTION IN THE
WEST INDIES.

THE following is the complete analysis of the sample of volcanic dust which fell over the Barbados on May 8th. It was collected and sent by a correspondent to Mr. Donald F. Mackenzie, a gentleman well known in West Indian circles. The partial analysis appeared in our issue of May 30th last.

SiO ₂		51'60
Al ₂ O ₃		21'12
Fe ₂ O ₃		9'28
CaO		9'07
MgO		3'96
Na ₂ O		0'59
K ₂ O		0'81
SO ₃		0'89
P ₂ O ₅		0'19
Loss on ignition		1'20
Undetermined		1'29

100 00

We are also able to give the complete analysis of the dust from the explosion of Mont Pelée, Martinique:—

SiO ₂		53'40
Al ₂ O ₃		21'00
Fe ₂ O ₃		9'50
CaO		9'70
MgO		2'00
Na ₂ O		2'33
K ₂ O		0'85
SO ₃		0'90
P ₂ O ₅		0'25

99'93

The above analysis was made on a sample dried at 105°, and is of special interest as it was collected from the deck of the S.S. *Roddam* on her arrival at St. Lucia; she was the only ship which escaped from St. Pierre after the eruption.

We regret that we are unable to give the analysis of the dust collected at Roxborough, Grenada, about 90 miles from La Soufrière, St. Vincent; the sample is so small that none can be spared for analysis.

HARD TOOL-STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

IT is well known that not many brands of hard tool-steel can be used with advantage and economy for the preparation of various cutting tools used in the machining of modern armour plates.

I have prepared for such purposes a tool-steel having the following composition:—

	Per cent.
Tungsten	2'00
Molybdenum	0'50
Carbon	0'90
Manganese	0'20
Silicon	0'18

The phosphorus and sulphur must be kept down as low as possible, on the average not more than 0'03 per cent of the combined elements, out of which not more than 0'01 per cent should be sulphur.

The steel was, and must be, prepared by the crucible process.

Such a self-hardening tool-steel is very convenient for the machining of hard metals.

N W Admiral's, St Petersburg, June 6, 1902.

THE
RADIO-ACTIVITY OF THORIUM COMPOUNDS.I. AN INVESTIGATION OF THE RADIO-ACTIVE
EMANATION.

By E. RUTHERFORD, M.A., D.Sc.,
Macdonald Professor of Physics, McGill University, Montreal,
and
FREDERICK SODDY, B.A. (Oxon.),
Demonstrator in Chemistry, McGill University, Montreal.

(Continued from p. 272).

The Chemical Aspect of the Question.

THE foregoing furnishes a short review of the physical side of the question at the present time. With regard to the chemical aspect, this has so far not been studied. The photographic method, almost the only one that has until now been used by chemists in the study of radio-activity, is not one which allows of the recognition and differentiation of an emanation as a component factor in producing the phenomena. The photographic method is of a qualitative rather than a quantitative character; its effects are cumulative with time, and as a rule long exposures are necessary when the radio activity of a feeble agent like thoria is to be demonstrated. In addition, Russell has shown that the darkening of a photographic plate is brought about also by agents of a totally different character from those under consideration, and, moreover, under very general conditions. Sir William Crookes (*Proc. Roy. Soc.*, 1900, lxvi., 409) has sounded a timely note of warning against putting too much confidence in the indications of the photographic method of measuring radio-activity. The uncertainty of an effect produced by cumulative action over long periods of time quite precludes its use for work of anything but a qualitative character.

Two or three chemists have studied the radio-activity of thoria, using the photographic method, without, however, distinguishing between the radio-activity due to the emanation and that due to the thoria itself. Sir William Crookes (*loc. cit.*), who succeeded by an elegant method in separating and isolating the radio-active constituent of uranium, also describes some experiments on thorium compounds with the same object, but did not succeed in effecting a separation. A method based on the fractional precipitation of the sulphate failed completely, but another method, the fractional crystallisation of the nitrate, gave preparations showing a difference in their photographic actions in the ratio of one to three. According to slight variations in the method employed, as, for example, whether a glass or a card bottom was used for the cell containing the substance to be tested (and both seem to have been employed), the radiation from the emanation would or would not contribute largely to the photographic action observed.

Debierne (*Comptes Rendus*, 1900, cxxx., 906), working on a very large scale, obtained from pitchblende, by using reactions which would lead to the separation of thorium, a material different in its chemical properties from radium (barium) and polonium (bismuth), but consisting in great part of thorium. This preparation was 100,000 times more active than uranium, and he therefore assumed the existence of a new element, "actinium," therein. He hazarded the suggestion that the radio-activity of thoria is due to the presence of the same substance, and derived support for this view from the recent work of one of us on the radio-activity of thoria, although on what grounds is not clear.

In the course of their work on the atomic weight of thorium, Brauner (*Trans. Chem. Soc.*, 1898, lxxiii., 951) and Baskerville (*Journ. Am. Chem. Soc.*, 1901, xxiii., 761), have obtained evidence of the presence of a foreign substance associated with thorium. The latter noticed that the separation, as he interpreted it, of this impurity reduced the photographic action considerably, and he concluded

that the pure material would be without photographic action. He employed a modification of Crookes's photographic method, but it cannot be decided with certainty from the description whether the radiation from the emanation would be eliminated or not.

The present work is concerned primarily with the radio-active emanation, although, of course, frequent occasion has arisen to examine correspondingly the ordinary radiation also. The methods employed are of an electrical character, based on the property generally possessed by all radiation of the kind in question, of rendering a gas capable of discharging both positive and negative electricity. These, as will be shown, are capable of great refinement and certainty. An ordinary quadrant electrometer is capable of detecting and measuring a difference of potential of at least 10^{-2} volts. With special instruments, this sensitiveness may be increased a hundredfold. An average value for the capacity of the electrometer and connections is 3×10^{-5} microfarads, and when this is charged up to 10^{-2} volts, a quantity of electricity corresponding to 3×10^{-13} coulombs is stored up. Now in the electrolysis of water 1 grm. of hydrogen carries a charge of 10^4 coulombs. Assuming, for the sake of example, that the conduction of electricity in gases is analogous to that in liquids, this amount of electricity corresponds to the transport of a mass of 3×10^{-18} grms. of hydrogen; that is, a quantity of the order of 10^{-12} times that detected by the balance. For a more delicate instrument, this amount would produce an inconveniently large effect.

The effects under investigation, from the nature of their manifestation, may well be, and probably are, produced by quantities of matter of the order of magnitude described, and therefore altogether beyond the range of the balance. But to assume on that account that the subject is beyond the pale of profitable chemical investigation is needlessly to limit the field of chemical inquiry. Although surpassing the spectroscope as a detective agent, as a quantitative instrument the electrometer is little inferior in accuracy to the balance. To take as an example the case of thorium mixed with zirconia, the former could be detected and accurately measured by means of its emanation with an electrometer, even although it were only present to the extent of one part in many thousands. A distinction must be made here between *emanation* and *emanating power*. The quantity of the former is what is measured by the electrometer. To express this in terms of weight, the emanating power, that is, the quantity of emanation produced by a given weight of the substance in question, must be known. As will be shown, this value varies with the previous history and present condition of the substance.

The electrometer also affords the means of recognising and differentiating between the emanations of different chemical substances. By the rate of decay, the emanation from thorium, for example, can be instantly distinguished from that produced by radium, and although a difference in the rate of decay does not of itself argue a fundamental difference of nature, the identity of the rate of decay furnishes at least strong presumption of identity of nature.

In the sense that has just been explained, the electrometer can be said to supply the investigation of the property of emanation with methods, so to speak, of quantitative and qualitative analysis which are simple and direct, and there is therefore no reason why the property in question, and even the nature of the emanation itself, should not be the subject of chemical investigation.

Scope of Work.

Of the great number of questions which immediately present themselves for answer in an investigation of this kind, the following are at present claiming our more immediate attention:—

1. Is the power of producing an emanation a specific property of thorium, or is it to be ascribed to the presence of a foreign substance, possibly in minute amount,

associated with it and amenable to chemical methods of separation?

2. Can the emanating power of "de-emanated" thorium be regenerated by chemical means? It has been mentioned that thorium, when intensely ignited, loses to a very great extent its power of giving an emanation. If such de-emanated thorium be subjected to a series of chemical changes, will it regain its emanating power or not?

3. Does the emanation or radio-active gas itself possess any property which would associate it chemically with any known kind of gravitational matter?

4. Is it possible to detect, by means of the balance, any loss in weight corresponding to the continuous emission of the emanation or any gain in weight of bodies rendered radio-active thereby?

5. Does the chemistry of thorium present any peculiarity capable of being connected with its almost unique power of producing an emanation?

To interpret rightly the results obtained, a more or less complete study of the effect of chemical and physical conditions on the emanating power is necessary. The effect of the state of aggregation, the presence or absence of water, the influence of light, temperature, the nature of the surrounding atmosphere, the lapse of time since preparation, &c., on the emanating power, as well as the differences in this property exhibited by different compounds, have been investigated.

The present communication does not attempt a full answer to all the above questions. The results so far obtained in answer to the first three will be presented. The work on the fourth is in progress, whilst the results of the investigation of the fifth question will be most conveniently given later in a separate communication.

Electrometer Method of Measuring Emanating Power and Radio-activity.

The term radio-active is now generally applied to a class of substances, like uranium, thorium, radium, and polonium, which have the power of spontaneously giving off radiations capable of passing through thin plates of metal. The radiations are in some cases very complex, but in the case of the substances mentioned, a portion at least of the radiation is similar in all respects to easily absorbed Röntgen rays. The characteristic and general property possessed by these radiations is to produce, from the gas through which they pass, positively and negatively charged carriers, which in an electric field travel to the negative and positive electrodes respectively. In this way, a small current is able to pass through a gas exposed to the radiations, even with a very weak electric field, and the measurement of this current by means of the electrometer affords a means of comparing the intensities of radiation.

As has been mentioned, compounds of thorium (and radium), in addition to radiations which travel in straight lines, emit radio-active emanations, which behave in all respects like a temporarily radio-active gas, and diffuse rapidly through porous substances, as, for example, thick cardboard, which are completely opaque to straight line radiation. Each particle of the emanation behaves as if it were a radiating centre, producing charged carriers throughout the gas in its neighbourhood. The emanation passes through plugs of cotton-wool, and can be bubbled through liquids without appreciable loss of radio-activity, whereas the charged carriers, produced by the emanation in common with the straight line radiation from radio-active substances on the contrary, completely disappear on passing through a plug of cotton- or glass-wool, or by bubbling through liquids. The means of eliminating the effects of the straight line radiation and of measuring the amount of the emanation alone thus suggest themselves. Air passed over uranium or other non-emanating radio-active substance will no longer conduct a current after passage through cotton-wool. The conductivity in the case of thorium, however, will persist, and afford a measure of the amount of emanation present.

Fig. 1 shows the experimental arrangement for com-

paring the emanating power of substances. These are placed in the form of fine powder in a shallow lead vessel inside the glass cylinder, c, 17 c.m. in length and 3.25 c.m. in diameter, provided with indiarubber corks. A current of air from a large gas bag, after passing through a tube containing cotton-wool to remove dust particles, bubbled through sulphuric acid in the vessel, a. It then passed through a bulb containing tightly packed cotton-wool to prevent any spray being carried over. The emanation mixed with air was carried from the vessel, c, through a plug of cotton-wool, d, which completely removed all the charged carriers carried with the emanation. The latter then passed into a long, brass cylinder, 75 c.m. in length and 6 c.m. in diameter. The cylinder insulated on paraffin blocks was connected to one pole of a battery of small lead accumulators, the other pole of which was connected to earth. Three electrodes, E, F, H, of equal length were placed along the axis of the cylinder, supported by brass rods passing through ebonite corks in the side of the cylinder. The current through the gas, due to the presence of the emanation, was measured by means of a Kelvin quadrant electrometer of the White pattern. The electrometer and the connections were suitably screened by means of wire gauze connected to earth. An insulating key was arranged so that either of the electrodes, E, F, H, or all of them together, could be rapidly connected to one pair of quadrants of the electrometer, the other two being always connected to earth.

When there is a very small increase for a large additional voltage. This is one of the most characteristic properties of conducting gases. For small voltages, only a small proportion of the charged carriers reach the electrode, on account of their re-combination throughout the volume of the gas. When the electric field is increased until all the carriers reach the electrode before any appreciable re-combination can occur, the current is at a maximum, and remains constant for large increases of voltage, provided, of course, that the electric field is below the value necessary for a spark to pass. In the experimental case, a pressure of 50 volts was found sufficient to give the maximum current between the electrodes.

This property of conducting gases allows us at once to make sure that the insulation of the electrodes is perfect at all stages of a long experiment; 100 volts applied instead of 50 to the cylinder should give the same current if the insulation is unaffected.

Rate of Decay of the Radiation from the Emanation.—The three electrodes, E, F, H, were used to compare the "rates of decay" of the radiations from the emanations of different substances. In the previous papers quoted, it has been shown that the radiating power of the thorium emanation falls to half its value in about a minute. In consequence of this, the current observed for the electrode E is greater than for electrode H. Knowing the velocity of the current of air along the cylinder and the respective currents to the electrodes E, F, H, the rate of decay of the

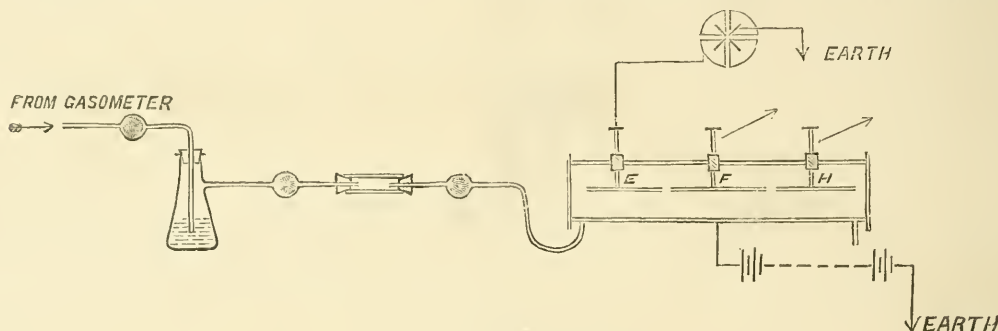


FIG. 1.

The insulation of the electrodes was first tested by sending a current of air through the apparatus without any emanating material in c. The rate of movement of the electrometer needle was accurately observed. On placing the emanating substance in c and continuing the air current for several minutes at a constant rate, the current due to the emanation reached a steady state. On separating the quadrants of the electrometer, the deflection from zero increased uniformly with time. The time taken to pass over 100 divisions of the scale was observed with a stop-watch. The number of divisions passed over per second may be taken as a measure of the current through the gas.

With this apparatus, the emanation from 10 grms. of ordinary thorium oxide produces a current of 3.3×10^{-11} ampères between the three electrodes connected together and the cylinder. With the electrometer working at average sensitiveness, this corresponded to a deflection of 100 divisions of the scale in twelve seconds, so that one-hundredth part of this current could be readily measured; that is, the emanation produced by one-tenth of a grm. of thorium oxide.

An electrometer one hundred times more sensitive than this failed to detect the presence of an emanation or radio-activity in the oxides of tin, zirconium, and titanium, the other elements of the same group in the periodic table.

Variation of the Current with Voltage.—The current through the gas observed with the electrometer at first increases with the voltage, but a stage is soon reached

radiation can be readily deduced. If, however, we merely require to compare the rate of decay of one emanation with another, it is only necessary to compare the ratio of the currents to the electrodes E, F, H in each case, keeping the current of air constant. If the ratio of the currents is the same we may conclude that the radiating power of each diminishes at the same rate. The comparison of emanation is thus rendered qualitative as well as quantitative. In most of the experiments, the current to the electrode E was about twice that to the electrode H; the velocity of the current of air along the cylinder was thus about 0.8 c.m. a second.

Comparison of Emanating Power.—The experiments in all cases on the amount of emanation from different substances are comparative. The standard of comparison was usually a sample of 10 grms. of thorium as obtained from the maker, which gave out a conveniently measurable quantity of emanation. Preliminary experiments were made to find the connection between the weight of thorium and the amount of emanation as tested in the cylinder. The following numbers show that the amount of emanation is directly proportional to the weight of the substance:—

Weight of thorium. Grms.	Divisions of scale per second.
2	1'41
4	2'43
10	6'33
20	13'2

This result shows that within the limit of accuracy desired we may take the amount of emanation as directly proportional to the weight of the substance. The determinations in the above table were made with the three electrodes connected together with the electrometer, and with a constant flow of air. The lead vessel in which the thorium was placed was 7.4 by 3.5 c.m. in area and 3 m.m. deep. In the comparison of emanating power, the maximum current between the electrodes for the standard 10 grms. of thorium was first observed. This was removed, and a known weight of the specimen to be tested was substituted, and the deflections again observed after the conditions had become steady.

If d_1 = No. of divisions per sec. for a weight, w_1 , of thorium;
 d_2 = No. of divisions per sec. for a weight, w_2 , of the specimen;

then—

$$\frac{\text{Emanating power of specimen}}{\text{Emanating power of thorium}} = \frac{d_2 w_1}{d_1 w_2}$$

The values d_1 and d_2 are corrected, when necessary, for natural leakage; that is, the current which passes under similar circumstances when no emanating material is present. This current is chiefly made up of a leakage due to conduction over the ebonite, as well as the current produced by the excited radio-activity which has collected on the negative electrode during the course of the day's experiments. It is generally very small, and the correction is only necessary when a specimen of substance almost free of emanation is being tested.

An example taken at random from the note-book will serve to illustrate the method of calculating the results, the emanating power of the comparison sample being considered 100 per cent :—

Dec. 7th, 11 a.m.—Natural leakage	10 divisions in 50"
	0'20 " 1"
5 grms. comparison sample ThO ₂	100 " 23'5"
3'6 " ThO ₂ ignited twenty-four	
hours over Bunsen burner in	
platinum crucible 	50 " 35'2"
d_1 = 4'25, corrected for nat. leak-	
age =	4'05
d_2 = 1'42 =	1'22

$$\frac{d_2 w_1}{d_1 w_2} = 0'42, \text{ or } 42 \text{ per cent.}$$

(To be continued).

CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS OF THE YTTRIUM GROUP.*

I.

By L. M. DENNIS and BENTON DALES.

(Continued from p. 266).

Experimental.

IN 1877 J. W. Mallet published an article on sipylite, a new niobate, from Amherst County, Virginia (*Am. Journ. Sci.*, 1877, xiv., 397). An analysis of the mineral made under his direction by W. G. Brown indicated the substance to be essentially a niobate of erbium containing some tantalum acid, about 1 per cent of yttrium oxide, and approximately 11.5 per cent of the earths of the cerium group.

In the following year Delafontaine (*Comptes Rendus*, lxxxvii., 933) examined this mineral and stated that it contained erbium, philippium, and ytterbium, the last-named element having been isolated but a short time before by Marignac.

A supply of sipylite which had been procured by one of us from Virginia and Texas was used as the source of the earths in this investigation. The mineral was finely

powdered and was then mixed with a large excess of primary potassium sulphate, and this mixture was fused in deep iron dishes in a crucible furnace. When decomposition was complete, the mass was cooled, powdered, and thrown into ice-water, the water being stirred until complete solution of all soluble compounds had been effected. The clear supernatant liquid was then syphoned off, nearly neutralised with ammonia, and precipitated with oxalic acid. The oxalates were then washed, dried, ignited, dissolved in sulphuric acid, and precipitated with ammonium hydroxide. This precipitate, after thorough washing by decantation, was dissolved in nitric acid, and to the neutral solution there was then added a saturated solution of potassium sulphate and crystals of the same salt. The mixture was violently stirred until the supernatant liquid failed to show the absorption bands of didymium. The resulting precipitate of the earths of the cerium group was removed by filtration, and was washed with a saturated solution of potassium sulphate. The filtrate was diluted with water and was precipitated by a solution of oxalic acid. These mixed oxalates, which, of course, still contained traces of the earths of the cerium group, were dried and ignited. The resulting mixture of oxides weighed about 350 grms. and was of a deep orange-yellow colour.

The atomic weight of the oxide mixture, assuming that all the oxides present were of the R₂O₃ type, was determined by the oxalate method of Gibbs and the sulphate method of Krüss, and was found to be in the neighbourhood of R^{III} = 108. Assuming that the average atomic weight of the elements other than yttrium lies in the neighbourhood of 165, this result shows that the mixture consists largely of yttrium oxide, approximately 75 per cent. The absorption spectrum when observed through a 10 c.m. layer of the saturated solution of the nitrate of the mixture showed the bands tabulated. The measurements in the table coincide with the maximum intensities of the absorption bands unless otherwise indicated.

[A description of the grating spectroscopy and method of measuring the absorption bands, is here omitted].

The Determination of the Atomic Weights of the Elements.

The method described by Gibbs (*Am. Chem. Journ.*, xv., 547) was used when only an approximate result was desired. The procedure was as follows:—A neutral or only very slightly acid solution of the earths whose atomic weight is to be determined is diluted with water, brought nearly to the boiling-point, and is then precipitated with a hot dilute solution of pure oxalic acid. The precipitate is washed by decantation and on the filter with hot water to remove the excess of oxalic acid, and is then dried at a temperature of 125°. A weighed portion of the oxalate precipitate is then converted to the oxide by ignition, and this oxide is weighed. Another weighed portion of the oxalate is dissolved in dilute sulphuric acid (1:8) and the oxalic acid is determined by titration with potassium permanganate. The atomic weight of the earths in the mixture of the rare earths is then easily calculated from the ratio of R₂O₃:C₂O₃. This method of determining the atomic weights gives results that are sufficiently accurate to enable one to judge of the progress of a method of separation or fractionation, but which are far from being exact; the comparison of the method with the sulphate method showed that the Gibbs procedure gave results differing by as much as four units from the sulphate method of Krüss. To ascertain the effect of changes in the conditions prevailing at the time of precipitation the following experiments were made:—

A solution of the earths was carefully freed from other elements by precipitating it with hydrogen sulphide, filtering off a very slight precipitate which formed, boiling the filtrate to remove the hydrogen sulphide, and precipitating it with ammonia, dissolving the washed precipitate in hydrochloric acid, and after nearly neutralising with ammonia precipitating this solution with oxalic acid. The

* *Journal of the American Chemical Society*, vol. xxiv., No. 5.

Angle.	Wave-length λ .	Element.	Description of band.
$12^{\circ} 2' 30''$	6832.4	{ Erbium Thulium	Faint, rather broad, edges vague.
$11^{\circ} 45' 10''$	6670.7	Erbium	Slightly stronger than 6832.4.
$11^{\circ} 29' 00''$	6519.9	{ Erbium	Moderately broad and strong, with two maxima; one in centre, the other at right edge.
$11^{\circ} 25' 20''$	6485.7	{	
$11^{\circ} 16' 40''$	6404.7	Holmium	Moderately strong; right edge sharp, maximum to right of centre.
$10^{\circ} 11' 50''$	5797.9	{ Didymium	Edges of broad, very hazy band. Scarcely visible.
$10^{\circ} 4' 03''$	5725.5	{	
$9^{\circ} 39' 50''$	5497.7	Unknown (Crookes)	Faint.
$9^{\circ} 30' 30''$	5410.0	Erbium	Broad strong band; two maxima, one to left of centre, the other at right edge.
$9^{\circ} 25' 30''$	5363.0	Holmium	Strongest band in spectrum; two maxima, one at left edge, the other in centre. Right edge indistinct.
$9^{\circ} 11' 10''$	5228.2	{ Erbium	Almost as strong as 5228.2. Extends from λ 4938.1 to λ 4825. Maximum to left of centre.
$9^{\circ} 6' 40''$	5185.9	{	
$8^{\circ} 32' 20''$	4862.7	Samarium	Very faint.
$8^{\circ} 17' 10''$	4719.8	Samarium	Very faint.
$8^{\circ} 11' 50''$	4669.5	Samarium	Almost as strong as 5228.2. Extends from λ 4550.0 to λ 4449.4.
$7^{\circ} 54' 00''$	4501.3	Dysprosium	Very faint.
$7^{\circ} 43' 40''$	4403.8	Didymium (?)	Faint and hazy.
$7^{\circ} 16' 50''$	4150.3	Samarium	

oxalates thus obtained were washed with very dilute hydrochloric acid (0.1 per cent) to remove iron, then with water, and were then dried, ignited, and the resulting oxides were dissolved in hydrochloric acid. This chloride solution was divided into two parts. One was precipitated with a hot and dilute solution of oxalic acid, while the other was precipitated in the cold and in more concentrated condition with a cold concentrated solution of oxalic acid. Another portion of the same original material was purified and treated in exactly the manner described above, and was divided and precipitated in the same way. The results of the atomic weight determinations of these various portions by the oxalate method were as follows:—

	Hot.	Cold.
I	111.28	108.26
2	105.06	104.70

The variations in these results show that they are greatly influenced by changes in the conditions, and that they by no means agree even when the same conditions prevail.

The other method employed for the determination of the atomic weights was that described by Krüss (*Zeit. Anorg. Chem.*, iii., 46). In this procedure the oxalate of the earth is placed in a porcelain crucible and ignited over a blast-lamp to constant weight. The crucible containing the oxide is placed on a water-bath, covered with a funnel, and the heating of the water-bath is continued until the water vapour has slowly and completely slaked the oxide. The substance is then dissolved in the crucible with dilute hydrochloric acid. A moderate excess of dilute sulphuric acid is added, and the solution is concentrated as far as possible on the water-bath. The excess of sulphuric acid is removed by placing the crucible on an iron plate 5 m.m. thick and heating the plate with a small Bunsen flame. This is continued until constant weight is obtained, and from the ratio of the oxide to the anhydrous sulphate, the atomic mass of the earth or earths present is calculated. Considerable difficulty was experienced in making duplicate analyses agree satisfactorily. The probable explanation of this trouble is to be found in the article by Brauner and Pavlicek (*Proc. Chem. Soc.*, xvii., No. 235, p. 63), in which those authors call attention to the fact that the sulphate which is finally weighed is liable to contain some acid sulphate. This acid sulphate is so stable that some of it remains undecomposed even at a temperature above 500° , while in other parts of the crucible it may have been partially broken down into a basic sulphate. They state that the error is greatest in the case of lanthanum, and

that it decreases as the basicity of the earth decreases. They determine the amount of sulphuric acid which is present in excess over the amount necessary to form the normal sulphate by dissolving the dry sulphates in water and titrating the free sulphuric acid with a twentieth normal solution of sodium hydroxide, using ethyl-orange as an indicator. The normal sulphate obtained by repeated crystallisation was found by them to be neutral to ethyl-orange.

These statements concerning the sulphates of the earths of the cerium group hold true for those of the yttrium group, but the error is less because the basicity of the earths of this group is less. For example, two weighed portions of a sulphate which had given $R^{III} = 115.90$ and 116.42 , were dissolved in water and the excess of free acid titrated as above, using methyl-orange as an indicator. The corrected results for these two samples were $R^{III} = 116.19$ and 116.47 . Another set which had given $R^{III} = 141.22$ and 141.53 gave after correction 141.51 and 141.73 . A third set giving $R^{III} = 107.31$ and 106.75 gave after correction 107.37 and 106.92 . There seems to be no regularity in the amounts of acid sulphate which are formed. The maximum error caused by its presence seems to be about 0.3 of a unit. All of the solutions which were tested showed an acid reaction, but in some cases a drop or two of the solution of sodium hydroxide was sufficient to neutralise the free acid. The results of duplicate determinations were usually brought to closer agreement by the introduction of the correction. In only one case was the opposite effect noted.

Experiments upon Methods for Separating Yttrium Group Earths.

The aim which the authors had in view in this work was not so much the isolation of one or another constituent of the mixture of the rare earths, but rather the study of various methods of separation to ascertain along what lines different treatments will cause the earths to separate. A complete systematic study of the different methods of separation was also not undertaken, for those procedures which give slow results and in which the successive treatments are of but slight effect upon the rare earth mixture, cannot be successfully employed, because of the time which is consumed and of the incompleteness of the separation which they bring about. Therefore, in the trials of the different methods to be described below it will be seen that the procedure was abandoned as soon as it became apparent that only slow separation was being effected.

(To be continued).

NOTICES OF BOOKS.

Les Nouveautés Chimiques pour 1902. Par C. POULENC, Docteur ès sciences. One vol., 8vo, 344 pp., 214 figures. Paris: J. B. Baillière and Son.

IN this volume we have, methodically arranged, new laboratory apparatus and methods applicable to scientific and industrial research. In the first chapter are collected together new appliances in physical chemistry, such as apparatus for determinations of density, high temperatures, fusion-points, &c.

The second chapter comprises apparatus for chemical manipulations, such as gas-burners, drying stoves, extraction apparatus, and appliances for the production of gases.

Chapter III. is devoted to electrical appliances used in chemical manipulations, such as regulators, make-and-break apparatus, transformers, volt-metres, &c.

The fourth chapter treats of analysis in general, then of gas analysis, metallurgical analyses, assay of commercial substances and articles of food, and medical analysis.

Finally, in the fifth chapter are collected together all appliances useful to bacteriology.

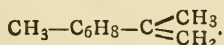
Chemists cannot fail to find in this volume much that will be useful to them in everyday work. There is a good table of contents and an exceptionally good index.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxiv., No. 20, May 20, 1902.

Hydrogenation of Ethylenic Carbides by the Method of Contact.—Paul Sabatier and J. B. Senderens.—It is apparent that the direct hydrogenation can only be effected by means of copper for the α -ethylenic carbides; that is to say, for those in which one of the CH_2 groups remains non-substituted. Styrolene or phenylethylene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, belongs to this class, and the authors recently showed that copper effects the transformation of this substance regularly into ethylbenzene. Limonene is generally supposed to possess the formula—

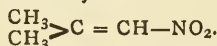


From this it can be predicted that copper cannot effect the hydrogenation of the cyclic radicle, but that it acts on the α -ethylenic branch. Such is found to be the case. Prolonged action of hydrogen towards 190° in presence of copper changes limonene into a carbide, $\text{C}_{10}\text{H}_{18}$, which boils at 170° and whose density d_4^{20} is 0.827. This carbide is violently attacked by nitrosulphuric acid. Hydrogenation in presence of nickel transforms it into methyl-paraisopropyl (cyclohexane); this latter being an isomer of the position of methane.

Action of Sulphites on Nitroprussiates. Bøedeker's Reaction.—Juan Fages.—To recognise the presence of sulphites the red colouration which they communicate to a solution of sulphate of zinc containing a little sodium nitroprussiate is employed. The addition of a little potassium ferrocyanide increases the sensitiveness of this reaction of Bøedeker. It is known that the property causing the formation of the red body belongs exclusively to the chemically neutral sulphite. Acid sulphites completely prevent the neutral sulphite from forming it. Consequently, to investigate a sulphite, the solution, if acid, must be neutralised, preferably with a neutral carbonate; free alkalis retarding the reaction. The author undertakes a careful examination of such reactions,

Volumetric Estimation of Iodides in presence of Chlorides and Bromides.—V. Thomas.—The author devises a new method of volumetric estimation of iodides in presence of chlorides and bromides by operating in presence of excess of a thallic salt. The iodine set free is eliminated by merely boiling the liquid. When all the iodine is got rid of, the non-reduced thallic salt is titrated. If a known quantity of thallic salt is used to start with and the difference expressing the quantity of TiCl_3 transformed into TiCl , the amount of iodide originally in the liquid can easily be deduced. This method of estimation of iodides is very exact and very rapid if a dilute solution of a thallic salt is employed.

A Gradual Method of Synthesis of Aldehydes.—L. Bouveault and A. Wahl.—By treating α -ethyl-nitrodimethylacrylate with sodium in presence of damp ether, or better with caustic alkalis at 50 – 60° , the authors succeeded in decomposing this substance into carbonic acid, alcohol, and a nitroisobutylene—



This synthesis has the advantage of determining the constitution of nitroisobutylene which Haitinger's preparation leaves doubtful. The authors intend to generalise this synthesis.

MISCELLANEOUS.

Science Abstracts.—The following Journals have been added since the beginning of 1902 to the list regularly dealt with in *Science Abstracts*, making a total at present of about 150:—

Journal of the Russian Physico-Chemical Society (Russian).
Proceedings of Academy of Sciences, Amsterdam (Dutch).
“ “ “ Stockholm (Swedish).
“ “ “ Christiania
“ “ “ (Norwegian).
Also “ “ “ Copenhagen (Danish).

Also—
Zeitschrift für Anorganischen Chemie.
Royal Society of Edinburgh Transactions and Proceedings.
British Optical Journal.
Elettricista (Rome).
Iron and Steel Institute Transactions.
American Society of Mechanical Engineers Transactions.
Engineering and Mining Journal (New York).
Power (New York).
American Telephone Journal.
La France Automobile.
Der Moterwagen.
Automobile Review (Chicago).
Archives of the Röntgen Ray.
Philosophical Society of Washington Bulletin.

The Solubility of Salts; the Iodates of Cobalt and Nickel.—A. Meusser.—Having taken up the study of these iodates the author finds that that of cobalt IO_3Co only exists in three forms:—(1) The blue-violet crystalline anhydride, forming in warm, very acid solutions; (2) that with $2\text{H}_2\text{O}$, in red-violet crystalline crusts; and (3) that with $4\text{H}_2\text{O}$, in crusts formed of hexagonal prisms. These two latter hydrates have solubilities increasing with the temperature, which is contrary to that of the anhydrous salt which decreases with the temperature. The anhydrous salt once formed only shows a feeble tendency to become hydrated. Facts very similar to these are observed with the nickel salt, IO_3Ni , which is also obtained in the anhydrous form in small, pale-yellow needles; then with $2\text{H}_2\text{O}$, but under different forms, one in green spherocrystalline crusts forming at 25 – 30° , the other at 50° , in small brilliant prisms; finally, with $4\text{H}_2\text{O}$ at 0 – 10° in hexagonal prisms. The curves of solubility have the same direction as those of the corresponding salts of cobalt.—*Berichte*, vol. xxxiv., p. 2432.

The Solubility of Salts. The Chromates of Calcium.—F. Mylius and J. von Wrochem.—A solution of CrO_4Ca in an excess of CrO_3 , evaporated in a desiccator, gives a tetrachromate, $\text{CaO} \cdot 4\text{CrO}_3 + 6\text{H}_2\text{O}$, in the form of very soluble, deep red crystals. The dichromate, $\text{Cr}_2\text{O}_7\text{Ca}$, crystallises with 3 H_2O , and also with 4 H_2O ; this latter hydrate is a new one, and occurs in beautiful orange-coloured prisms. At the other end of the series there appears a basic chromate, $2\text{CaO} \cdot \text{CrO}_3$, already described by M. von Foullon; but the most important one is the neutral chromate CrO_4Ca , which can exist in several different degrees of hydration, of which the following are the solubilities at 18° :—

	Density of the saturated solutions.	Molecules of the salt per 100 mols. of water.
Hydrate with 2 H_2O (α - clino-rhombic variety .	1.149	1.93
Hydrate with 2 H_2O (β - ortho-rhombic variety .	1.105	1.33
Hydrate with H_2O ..	1.096	1.22
Hydrate with $\frac{1}{2}$ H_2O ..	1.044	0.51
The anhydrous salt ..	1.023	0.27

The hydrate $2\text{H}_2\text{O}$, variety α , is in very small crystals, macted like gypsum, with which it is isomorphous. It is very unstable, and has a tendency to pass to the β form or to one of the lower hydrates spontaneously. The hydrate $\frac{1}{2}\text{H}_2\text{O}$ corresponds to a product of heating gypsum, and is obtained by rapidly heating the 15 per cent solution of CrO_4Ca , treated with CaCl_2 or with glycerin, to 100° . It has the appearance of chloroplatinate of ammonium; it does not lose its water below 400° . The solubility of the different hydrates decreases fairly rapidly with the temperature.—*Berichte*, vol. xxxiii., p. 3689.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

River Water.—If Mr. Ernest A. Lewis cares to communicate with me I can give him the potable analysis of two samples of South and West Jaquel I did in 1897.—LEO TAYLOR, F.I.C., 31, Moorgate Street, London, E.C.

Extraction of Oil from Seeds.—Can any reader recommend a good book dealing mainly with the extraction of oil from seeds by hydraulic pressure? I have Thorpe's "Dictionary," Grove and Thorpe's "Technology," Alder Wright's "Soap," and Hurst's "Oils, &c.," but they do not give sufficient detail.—SEED CRUSHING.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Chemical, 5.30. Ballot for the Election of Fellows. "Elimination of a Ni ro-group on Diazotisation—Dinitro-*p*-anisidine," by R. Meldola and J. V. Eyre. "A New Type of Substituted Nitrogen Chlorides," by F. D. Chattaway. "The Colour Changes exhibited by the Chlorides of Cobalt and some other Metals, from the Standpoint of the Theory of Electro-affinity," by F. G. Donnan and H. Bassett, jun. "An Accurate Method of Determining the Compressibility of Vapours," by B. D. Steele. "The Molecular Condition of Borax in Solution," by H. S. Shelton. "Preliminary Notice of some New Derivatives of Pinene and other Terpenes," by W. A. Tilden and H. Burrows. "The Preparation of Pure Chlorine and its Behaviour towards Hydrogen," by J. W. Mellor and E. J. Russell. Microscopical, 8. "The Genus *Synchaeta*," by C. F. Roussetlet.

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THE CHEMICAL NEWS.

VOL. LXXXV., No. 2221.

COEFFICIENTS OF THE CUBICAL EXPANSION OF ICE, HYDRATED SALTS, SOLID CARBONIC ACID, AND OTHER SUBSTANCES AT LOW TEMPERATURES.*

By JAMES DEWAR, M.A., D.Sc., LL.D.,
Jacksonian Professor, Cambridge University, and
Fullerian, Royal Institution, London.

(Concluded from p. 279).

Notes on the Results of Table I.

SODIUM, extending down to low temperatures, has a coefficient about the same as that of mercury at the ordinary temperature. The coefficient for sulphur is about half of

* A Paper read before the Royal Society, May 1, 1902.

that between 0° and 100°, being 0.0002237, and that of iodine is not far removed from the value 0.000285 given for the solid at ordinary temperatures. The rate of expansion of liquid iodine is about three times this value. Paraffin ought to have a value of 0.0004633 from Fizeau, but Rodwell's coefficient between 0° and 38° is 0.00035. The value found for naphthalin is about half that of the liquid near its melting-point, viz., 0.000785. If the liquid coefficient be taken at a corresponding temperature to that of the liquid carbonic acid when comparing it with the solid, then its value is 0.001213, or the coefficient would be now in the ratio of 4 to 1. The graphite calculated from Fizeau should be 0.0000929, which is greater than my value; but the samples were different. My two specimens of chloride of ammonium gave nearly the same value, and the result is in agreement with that found by Playfair and Joule, viz., 0.000191. If a Fizeau coefficient for this salt is calculated, the value is 0.0000761, which in this case is far too small. The coefficient found for oxalic acid is again only a little smaller than that given by Playfair and Joule, viz., 0.0002748. As regards the hydrated salts, phosphate of soda, hyposulphate of soda, and

TABLE I.

	A-C.	A-B.	D.	d.†	d ₁₇ .	a ⁰⁰⁰⁰
Sulphate of aluminium (18)*	45.338	26.961	1.0225	1.7194	1.6913	0811
Biborate of soda (10)	47.057	28.328	1.0405	1.7284	1.6937	1000
Chloride of calcium (6)	68.942	37.493	0.9347	1.7187	1.6775	1191
Chloride of magnesium (6)	36.663	22.438	0.9816	1.6039	1.5693	1072
Potash alum (24)	50.462	30.177	0.9816	1.6414	1.6144	0813
Chrome alum (24), large crystal ..	47.345	26.406	1.0226	1.8335	1.8199	0365
Chrome alum (24)	40.147	23.665	1.0517	1.7842	1.7669	0478
Carbonate of soda (10)	55.675	34.863	0.9347	1.4926	1.4460	1563
Phosphate of soda (12)	57.085	35.848	0.9700	1.5446	1.5200	0787
Hyposulphate of soda (5)	53.121	28.836	0.9573	1.7635	1.7290	0969
Ferrocyanide of potassium (3)	55.914	29.115	0.9887	1.8988	1.8533	1195
Ferricyanide of potassium	68.902	35.961	0.9887	1.8944	1.8109	2244
Nitro-prusside of sodium (4)	49.614	28.526	0.9887	1.7196	1.6803	1138
Chloride of ammonium, sample i... ..	34.530	21.032	0.9597	1.5757	1.5188	1820
Chloride of ammonium, sample ii. .	31.083	18.870	0.9597	1.5809	1.5216	1893
Oxalic acid (2)	23.644	13.293	0.9571	1.7024	1.6145	2643
Oxalate of methyl	56.465	37.760	1.0217	1.5278	1.4260	3482
Paraffin	15.675	16.031	0.9992	0.9770	0.9103	3567
Naphthalin	43.622	33.001	0.9347	1.2355	1.1589	3200
Chloral hydrate.. ..	53.321	26.436	0.9789	1.9744	1.9151	1482
Urea	42.811	32.326	1.0282	1.3617	1.3190	1579
Iodoform	140.012	32.381	1.0282	4.4459	4.1955	2930
Iodine.. ..	17.806	4.135	1.137	4.8943	4.6631	2510
Sulphur	25.499	13.813	1.137	2.0089	2.0522	1152
Mercury	77.719	5.135	0.9502	14.382	14.193†	0887
Sodium	16.904	16.504	0.9818	1.0066	0.972	1865
Graphite (Cumberland)	22.221	9.986	0.9573	2.1302	2.0990	0733

* The figures () refer to the number of molecules of water of crystallisation.

† Density at the temperature of liquid air.

‡ At -38.85°.

TABLE II.—Ice.

Silver ball. Weight lost in— 1. Oxygen; 2. Liquid air.	Density of liquid air.	Weight of ice and copper ball and wire.		Weight of copper ball and wire.		Weight of ice in vacuo.	Density of ice at -188.7° C.
		Gaseous air at -188.7° C.	Liquid air at -188.7° C.	Air at 16° C.	Liquid air -188.7° C.		
1. 14.411	0.9820	47.080	33.430	38.075	33.933	9.0612	0.93032
2. 12.446							
1. 14.409	0.9502	46.78	33.88	38.128	34.103	8.706	0.92646
2. 12.042							
1. 14.407	0.9942	56.391	32.740	38.127	33.94	18.167	0.93318
2. 12.597							

TABLE III.—Solid Carbonic Acid.

Weight of solid CO ₂ .		Density of liquid air.	Weight in vacuo.	Density at -188.8° C.
Gaseous air at -188.8° C.	Liquid air at -188.8° C.			
19.865	7.905	0.9832	19.919	1.6308
22.55	9.37	0.9502	22.61	1.6226

[illegible]

CONTRIBUTIONS TO THE CHEMISTRY OF THE
RARE EARTHS OF THE YTTRIUM GROUP.*

I.

By L. M. DENNIS and BENTON DALES.

(Continued from p. 286).

Fusion of the Yttrium Group Nitrates with Alkali Nitrates.

THE method first tried was that of fusion of the rare earth nitrates with alkali nitrates, proposed by Debray, and which, as modified by Dennis and Magee (*Journ. Amer. Chem. Soc.*, xvi., 653), gives such satisfactory results in separating cerium from the other members of the group. It was hoped that the decomposition points of some of the yttria group double nitrates might be found sufficiently far apart to admit of a sharp separation, but such was not the case.

The dry yttrium group nitrates were mixed with six times their weight of a molecular mixture of potassium and sodium nitrates, placed in a deep porcelain evaporator, and fused in a large double air-bath, the space between the walls of the bath being filled with infusorial earth to prevent radiation. Three fusions were made, and after each the substance was extracted with hot water, yielding an insoluble and a soluble portion. Fusions were made at three temperatures, 280°, 320°, and 360°, using different mixtures each time. These temperatures were measured by means of a Le Chatelier pyrometer manufactured by Keiser and Schmidt, of Berlin. Each portion was fused for about three hours. The results were irregular, and gave no indication of a sharp separation by this method, as the following atomic weights show:—

Atomic weight of the initial metal mixture, 108.19.

Insoluble.	Temperature.	Soluble.
114.70	280°	108.31
127.55	320°	108.14
112.24	360°	102.43

A comparison of the absorption spectra of solutions of these portions and of the original material with a direct-vision spectroscope showed no appreciable differences.

Partial Precipitation with Hydrochloric Acid Gas.

PARTIAL precipitation of the anhydrous chlorides by hydrochloric acid gas from a cooled solution was next tried. A concentrated solution of the chlorides ($R_{III} = 107.94$) was placed in a gas wash-bottle surrounded by a freezing-mixture of ice and salt; hydrochloric acid gas from a Norblad generator was then passed through the liquid for about five hours. Quite a heavy white crystalline precipitate was obtained. This was thrown on to a porous plate and drained. It is very deliquescent. The concentrated solution of the crystals had a yellow colour. The mother-liquor changed colour from rose to orange while saturated with hydrochloric acid, due probably to the forcing back of the dissociation of the chloride by hydrochloric acid.

The mother-liquor was precipitated with ammonia and washed to remove chlorides, the precipitate dissolved in hydrochloric acid, concentrated, and again treated for two hours with hydrochloric acid gas in the freezing-mixture. Another heavy white crystalline precipitate was obtained, which gave a slightly yellow solution.

The spectra of the original solution and of saturated solutions of these two precipitates were compared by means of the small comparison spectroscope manufactured by Zeiss, of Jena, and described by Dr. Pulfrich in the *Zeitschrift für Instrumentenkunde*, October, 1901. No changes in the relative intensities of the various bands were visible.

Partial Decomposition of the Chromates.

Pattison and Clarke (*CHEM. NEWS*, xvi., 259) separated cerium from lanthanum and didymium by heating the normal chromates to 230° F. for some hours. The method when tried on this material gave no separation whatever. About 3 grms. of the oxides ($R_{III} = 103.75$) were dissolved in concentrated chromic acid, and the solution evaporated to dryness. The dry mass was heated for six hours at a temperature of about 200°, but decomposition merely on the surface was the only result, as could be told by the change in colour from the red of the chromate to the green of the chromic oxide. This same substance was then pulverised and heated for six hours to 250° with practically the same result. The substance was extracted with hot water, yielding a red solution and a greenish-black residue. The solution was evaporated to dryness, and was then heated to 300° for eight hours, but only very slight decomposition resulted. The insoluble greenish-black residue was again obtained from this portion. These two residues were treated with hot hydrochloric acid, and the green solution which was obtained was neutralised with ammonia, and precipitated with oxalic acid. Only a faint trace of the rare earth oxalates were thrown down.

Fractional Precipitation with Potassium Chromate.

THE first to use this method in the separation of the rare earths was Gerhard Krüss (*Zeit. Anorg. Chem.*, liii., 92). This has since been modified by Moissan (*Comptes Rendus*, cxxii., 573), and in this form was employed by the authors on the material which gave $R_{III} = 107.94$. Krüss added a neutral solution of potassium chromate to a neutral nitrate solution of the earths, while Moissan used a sulphate solution of the earths, neutralising the liquid with ammonium hydroxide before each fractional precipitation with potassium chromate. The authors followed Moissan's directions carefully, but used a solution of the nitrates of the rare earths instead of the sulphates. This nitrate solution, amounting to 15 litres and containing about 140 grms. of the oxides, was first neutralised with ammonium hydroxide, and 1 litre of the solution of potassium chromate containing 97 grms. to the litre was added with continual stirring. The precipitation was carried on in tall glass cylinders of about 10 litres' capacity. The flocculent precipitate was allowed to settle, and the red supernatant liquid was removed by means of a syphon. The precipitate was washed with water until the wash-water gave no precipitate with ammonium hydroxide. The earths in the wash-water were recovered by precipitation with ammonium hydroxide, and this precipitate was dissolved in nitric acid to a neutral solution, and was added to the mother-liquor. This liquid was then again carefully neutralised with ammonium hydroxide, and was then treated with the same amount of potassium chromate solution as was used for the first fraction. This procedure was repeated four times, giving in all five fractions. The mother-liquor and wash-water from the last fraction were precipitated by ammonium hydroxide yielding fraction 6. With each succeeding precipitation the dilution of the solution was increased by about 1 litre.

Precipitate 1 was so small in amount as to render its separate treatment inadvisable; it was therefore united to precipitate 2, and the two were treated as one fraction. Each precipitate was dissolved in dilute hydrochloric acid, the chromic acid was reduced by adding alcohol and heating on the water-bath, and the resulting green solution was then nearly neutralised with ammonia, heated to boiling, and precipitated with a boiling solution of oxalic acid. In each case the precipitated oxalates were washed with a 1 per cent solution of hydrochloric acid, and were then dried and ignited. The resulting oxide was dissolved in hydrochloric acid. For the atomic weight determinations by the Gibbs method a portion of each of these solutions was precipitated with oxalic acid, and the oxalate was washed and dried.

Fraction 1 gave a pink oxalate, a deep orange oxide, and its saturated solution of a brownish-yellow colour showed

* *Journal of the American Chemical Society*, vol. xxiv., No. 5.

the same absorption bands as the original solution, but the bands were slightly stronger.

Fraction 2 was practically identical with fraction 1.

Fraction 3 gave a pink oxalate and an orange-yellow oxide somewhat lighter in tint than the oxide from fraction 2. Its saturated solution showed all of the absorption bands strongly.

Fraction 4 yielded an oxide somewhat lighter in colour than that from fraction 3, and its solution showed the bands plainly, but not as plainly as the preceding fractions.

Fraction 5 gave an oxalate of a pale pink colour and a very light yellow oxide. The saturated solution of its oxide was much paler in colour than the solutions of the preceding fractions, and while it showed all of the absorption bands they were much less distinct than in fraction 4.

Fraction 6 gave a perfectly white oxalate, and the oxide showed only the faintest tinge of buff colour, and its solution had a pale greenish-yellow tint. The absorption bands of this last solution were quite weak.

The atomic weights of the original material and the six fractions with fractions 1 and 2 united are as follows:—

Original, 107.94.

1 and 2.	3.	4.	5.	6.
133.54	126.13	114.04	97.83	94.01

Fractions 1, 2, 3, and 4 were then united, and were again fractionally precipitated by the chromate method. The atomic weights of the three fractions thus obtained were 145.34, 127.38, and 103.75. The middle fraction was then split up into two parts, one showing an atomic weight of 150.03, and the other 124.53.

Fractions 5 and 6 contain yttria with about 10 per cent of oxides having high atomic weights as terbia, erbia, and ytterbia. These two fractions comprise nearly half the material used in the fractionation. After 7 grms. of oxides with metal atomic weight of 107.07 had been extracted from them by this same process, the rest was set aside as yttria material. The two highest fractions $R_{III} = 145.34$ and 150.03 were also set aside for future use.

It is thus seen that fractionation with potassium chromate separates the earths of this group with considerable rapidity. It is especially serviceable as a means of obtaining yttria free from the other earths, this substance being separated in quite pure form at the end of a comparatively short series of fractions. The mixture of oxides in the first fractions is still a very complicated one, and further application of the chromate method does not appear to affect it appreciably.

Fractional Precipitation with Primary Potassium Oxalate.

The separation of the earths with this method proceeds but slowly, as is shown by the atomic weights given below. The method is a modification of the one used by Delafontaine for the separation of terbia from yttria and erbia. He added the solution of primary potassium oxalate to a solution of the rare earths until a point was reached at which another drop of the reagent caused a permanent precipitate. The liquid was then allowed to stand until the oxalates crystallised out. The solid substance was then removed, and crystallisation was repeated after the addition of more of the oxalate.

The authors used very dilute solutions in carrying on this method of fractionation, that of the primary potassium oxalate being about one-twelfth molecular, while the solution of the rare earths was diluted until the absorption bands were just visible with distinctness. The solution of primary potassium oxalate was made by dissolving in water molecular proportions of potassium oxalate and oxalic acid.

In order to be able to judge of the effect of fractional precipitation by this method upon the absorption bands of the solution, the precipitation was carried on before the spectroscope. The solution of the rare earths was transferred to a large crystallising dish about 20 c.m. in diameter, and this dish was placed directly before the slit of a Steinheil grating spectroscope. Light was furnished by a Linnemann zircon-disk lamp. The solution was kept in

constant motion by means of a stirrer run by a Porter electric motor, and the solution of the primary potassium oxalate was added drop by drop from a burette. Before beginning the fractionation it is necessary to add a concentrated solution of the oxalate until a permanent precipitate just forms.

The first effect of the precipitation was to weaken the holmium bands, while all the bands decreased in intensity, the most persistent being the erbium band in the green. About 5 grms. of the oxides were obtained from fraction 1. Half of the mother-liquor from this fraction was then precipitated, and 6 grms. were obtained. This halving of the solution was made necessary because of the limited size of the dish, and concentration was undesirable because of the possible disturbing action of the more concentrated oxalate solution upon the earths. The mother-liquor from fraction 2 was again divided, and about 5 grms. of oxides were obtained in fraction 3. At the end of this third fraction all of the absorption bands had disappeared with the exception of the erbium band in the green, which was just visible. The mother-liquor from the last fraction amounting to one-fourth of the original solution was completely precipitated by the addition of the concentrated solution of primary potassium oxalate. Each of the precipitates was washed, dried, ignited, and dissolved in nitric acid. The oxalates of the first three fractions were pink, while that of the last one was white. The oxides of the first three fractions were orange-yellow in colour, while that of the last fraction had a pinkish tinge. All the solutions showed the rose-pink colour of erbium salts. In determining the atomic weights, a portion of each nitric acid solution was precipitated with ammonium hydroxide, and this precipitate was thoroughly washed with water to remove potassium salts. It was then dissolved in nitric acid to a barely acid solution, and precipitated with oxalic acid.

Original, 112.16.

1.	2.	3.	4.
118.80	116.71	111.08	102.53

The precipitates which are thrown down by these oxalate reagents are finely crystalline, and are consequently easily freed from the mother-liquor. Fractionation could probably be carried on with a fair degree of rapidity, and interesting results might be obtained. The separation was, however, too slow for the authors' purposes, and therefore no further trials have yet been made of it.

Fractional Decomposition of a Solution of the Mixed Nitrates by Means of an Electric Current.

About 120 c.c. of a solution of the nitrates ($R_{III} = 107.94$) were carefully neutralised with ammonium hydroxide. This solution was placed in a Classen platinum electrolysis dish, and was connected with the negative terminals of two cells of a storage battery. A platinum disk about 3 c.m. in diameter was used as the positive electrode. A low current of N. D.₁₀₀ = 0.17 to 0.42 ampère at a potential difference between electrodes of 2.2 to 2.7 volts was passed into the solution for about twenty hours, the solution being kept neutral and at room temperature (about 21° C.). A white precipitate of the hydroxides was obtained at the cathode. A brownish deposit collected on the anode, but this was found to be lead dioxide due to a trace of lead present in the solution. The solution was poured off from the precipitate, the latter adhering to the dish sufficiently to make it possible to wash it without loss. The solution was evaporated to its original volume, and was again submitted to electrolysis, with a current of N. D.₁₀₀ = 0.18 to 0.20 ampère at 1.8 to 1.9 volts for seven hours at 21° C. Again there was a small amount of precipitate formed. This being non-adherent, it was removed by filtration, and the wash-water and solution were again evaporated to the original volume and electrolysed. A current of N. D.₁₀₀ = 0.17 ampère failed to produce any further precipitation after six hours, so the current was raised to N. D.₁₀₀ = 0.33 to 0.42 ampère with a potential difference of 2.45 to 2.55 volts, and allowed to run for twenty-three hours. A further

white precipitate was obtained. These two precipitates were united for the second fraction; the atomic weight of the fraction was then determined, as was that of the first fraction and that of the residual solution. These three values compared with the original are as follows:—

Original, 107.94.		
1.	2.	Residual solution.
120.22	116.61	106.20

If the decomposition voltages of the rare earths of this group were far enough apart to permit of a separation by means of electrolysis, the two fractions here should have atomic weights which differ more than do these. For if the earth or earth mixture which is thrown out of solution by a current of N. D. 100 = 0.17 ampère at a potential difference between electrodes of about 2.5 volts was different from that which is precipitated by a current of about twice the density, the difference should show itself in the atomic weights. It is evident therefore that, under the conditions here prevailing, the separation of the rare earths can only slowly be affected.

Fractional Precipitation with Magnesia Usta.

Muthmann and Röllig (*Ber. d. Chem. Ges.*, xxxi., 1719) separate cerium in the quadrivalent condition from lanthanum and didymium by precipitation with powdered zinc oxide, and then separate lanthanum from didymium by partially precipitating the hot concentrated solution with magnesia usta until the absorption bands of didymium have disappeared.

The effect of magnesium oxide as a precipitant was tried with a nearly saturated neutral solution of the chlorides of these yttrium earths ($R^{III} = 104.4$). Muthmann states that he stopped the precipitation when the didymium absorption bands had just disappeared. The authors found, however, that while a precipitate formed easily it would not settle sufficiently to enable the absorption bands to be observed.

The solution of the chlorides was heated to boiling, and while in vigorous ebullition powdered magnesia was added in small quantities, with constant stirring. The precipitate which soon separated was first washed by decantation, and was then washed upon a filter with hot water. The mother-liquor and the four wash-waters were evaporated nearly to saturation, and the precipitation was repeated. A second repetition of this procedure gave a third fraction, and the mother-liquor and wash-waters from this were then precipitated with oxalic acid for the fourth and final fraction.

Each of the precipitates was dissolved in hydrochloric acid, and the solution was concentrated. These four solutions showed practically no variations in absorption bands when examined with a direct vision spectroscope. The solution from the first precipitate was treated with ammonium chloride and ammonium oxalate as Muthmann recommends, and the resulting precipitate was washed by decantation with hot water containing 0.1 per cent hydrochloric acid, and was then washed with water alone. The precipitate was free from magnesia, but contained iron. The oxalates were at first non-crystalline, and settled very slowly, but the addition of the dilute acid caused them to separate in crystalline condition. It was found that, by adding oxalic acid to the neutral chloride solution of these precipitates, complete precipitation of the rare earths could be obtained, and this precipitate was free from magnesia, provided ammonium chloride was present. This method of purification was therefore used with the other fractions. The oxalates from all four of the fractions were ignited and dissolved in hydrochloric acid. Since the resulting solution contained traces of iron, portions of each fraction were freed from iron by re-precipitation with oxalic acid, and the atomic weight determinations were made with this purified material. The atomic weights and absorption spectra showed that very little change had been caused in the earth mixture by fractional precipitation with magnesium oxide.

(To be continued.)

THE RADIO-ACTIVITY OF THORIUM COMPOUNDS.

I. AN INVESTIGATION OF THE RADIO-ACTIVE EMANATION.

By E. RUTHERFORD, M.A., D.Sc.,
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and

FREDERICK SODDY, B.A. (Oxon.),
Demonstrator in Chemistry, McGill University, Montreal

(Continued from p. 285).

Comparison of Intensity of Straight Line Radiation.

It was frequently of interest to obtain information about the intensity of the ordinary radiation correspondingly with measurement of emanating power. In order to do this rapidly and accurately, the following method was used. Fig. 2 shows the general arrangement. 0.1 grm. of the compound to be tested was reduced to fine powder and uniformly sifted over a platinum plate 36 sq. c.m. in area.

This plate was placed on a large metal plate connected to one pole of a battery of 300 volts, the other pole of which was earthed. An insulated parallel plate was placed about 6 c.m. above it, and the whole apparatus enclosed in a metal box connected to earth, to prevent electrostatic disturbance. The shaded portions in the figure represented insulators. A door was made in the apparatus so that the plate could be rapidly placed in position or removed. The current between the plates is observed in the usual way with the electrometer. The ratio of the currents for two substances is a comparative measure of their radio-activity. It is only possible to compare together with certainty substances of similar density and state of division,—a light, floury material will tend to give lower values than a dense powder.

If a substance gives off an emanation, the current between the plates increases with time. Under these conditions when the thorium is exposed in thin layers with a maximum of radiating surface, all but 1 or 2 per cent of the total effect is due to the straight line radiation; even when the effect due to the emanation has attained its maximum; this constitutes a very small percentage of the whole. This effect, however, may be to a large extent eliminated by taking the current between the electrodes immediately after the material is placed in the testing apparatus, or by passing a current of air between the electrodes to remove the emanation, and prevent it accumulating.

It is thus possible to compare intensity of radiations with an error not exceeding 1 or 2 per cent, and with great rapidity, and in these respects the electrical method is altogether superior to the photographic.

Comparison of Emanating Power.—The apparatus (Fig. 2) described for the comparison of radiations, can also be quite well employed for a comparison of emanating power. In this case, a thick layer of thorium (several grms.) is spread over the plate and covered with two thicknesses of ordinary paper. This has been found almost completely to stop the straight line radiation, whilst allowing the emanation to pass through unimpeded. The current is now measured when a steady state has been reached, due to the accumulation of the emanation. This takes some time, and draughts of air must be guarded against. For this reason, it is less convenient than the method first described, but the results obtained by the two methods are almost exactly the same. Thus a sample of "de-emanated" thorium which gave 12 per cent of the emanating power of the comparison sample by the first method gave 13 per cent by the second method, whilst a sample of oxide prepared from thorium oxalate gave 37 per cent and 39 per cent by the two methods respectively. The close agreement in the values by methods so completely different in character is a proof that the indications of the methods are worthy of a great degree of confidence.

The De-emanation of Thoria and the Regeneration of the Emanating Power.

The emanating power of thoria, as has been stated, is destroyed to a large extent by intense ignition. A closer study of this is the first step in the investigation of the phenomenon. Previous experiments had not succeeded in completely de-emanating thoria, although a reduction to about 15 per cent of its original value had been accomplished. A sample of this preparation which had been kept for two years had not altered from this value. An experiment was performed in which thoria was heated to the highest temperature which could be safely employed with platinum vessels: (1) in a thin layer in a large platinum dish, and (2) in bulk in a small platinum crucible placed inside the dish. The two were heated together by means of a powerful gasoline furnace for one hour. The temperature was such that the fireclay walls fused, and the pipeclay of a triangle showed signs of having been softened. It was found that the sample that had been heated in a thin layer in the dish retained about 16 per cent of its original emanating power, whilst the other sample retained about 8 per cent. There is thus no advantage in heating in thin layers, in fact, rather the reverse, for the sample showing 16 per cent again heated to a slightly lower temperature for half-an-hour in a small crucible was reduced to 12 per cent.

In another experiment, a small platinum crucible filled with thoria was heated for half-an-hour in a small furnace by a large blowpipe and powerful pair of bellows. Some

A sample of de-emanated thoria (retaining about 14 per cent) was placed in the middle of a Jena glass tube, one end of which was closed and contained water, the other end being drawn out to a jet. This was supported in a powerful tube furnace in a sloping position, and the part containing the thoria heated to the highest possible temperature, while a slow current of steam from the water at the end was passed over it, escaping by the jet. When all the water had evaporated, the jet was drawn off and the tube allowed to cool in an atmosphere of steam free from air. The thoria, on testing, was found to have been lowered in emanating power to about 7 per cent. The further heating had thus reduced the emanating power without the steam having at all regenerated it.

In the next experiment, the reverse process was tried. Two exactly parallel processes were carried out for ordinary thoria possessing the normal amount of emanating power. In the first, it was heated in a porcelain tube in the tube furnace for three hours, while about 500 c.c of water were distilled over it from a retort. In the second, another quantity of thoria was heated in exactly the same way for the same time, only a current of well dried air was substituted for the steam. The result was conclusive: each sample had had its emanating power reduced to exactly the same amount; that is, about 50 per cent of the original.

These experiments prove that water vapour exerts no influence either in de-emanating thoria or in effecting a recovery of its lost emanating power.

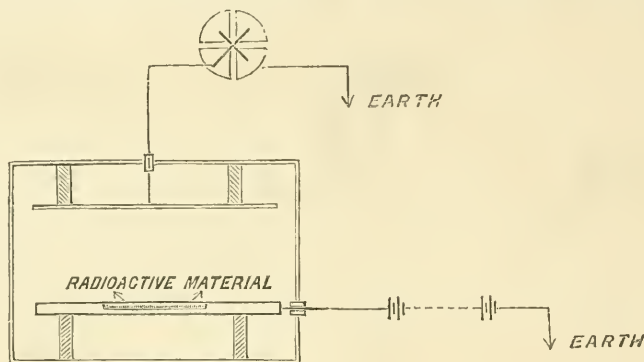


FIG. 2.

asbestos-wool had completely fused on the outside of the crucible, and the temperature was probably but little lower than in the previous experiment. This sample also retained about 8 per cent of its emanating power. No further attempt has yet been made to completely destroy the emanating power.

A small quantity of thoria heated in a platinum crucible in the open over an ordinary small sized blowpipe and bellows for five minutes retained about 45 per cent of its emanating power. The effect of time as well as of temperature was studied by heating about equal quantities in a platinum crucible over an ordinary Bunsen burner for different periods.

Heated to minutes	Emanating power =	61 per cent
" 1 hour	"	= 59 "
" 24 hours	"	= 42 "

It thus appears that there is a large and practically sudden decrease of emanating power for each temperature above a red heat, followed by a very gradual decrease with time when the temperature is maintained; thus five minutes on the blowpipe, whilst much more effective than the same time at the temperature of the Bunsen burner, produced rather less effect than twenty-four hours at the latter temperature.

Effect of Moisture.—The next point to be examined was whether the loss of emanating power could be attributed to a loss of water and desiccation of the thoria by ignition.

The Re-generation of the Emanating Power by Chemical Processes.—The task of subjecting de-emanated thoria to a series of chemical changes to see if it would recover its lost emanating power was then undertaken.

It may first be mentioned that thoria which has been subjected to ignition has changed very materially in chemical and physical properties. The pure white colour changes at temperatures corresponding to the first stages of de-emanation to a light brown, and after subjection to the very highest temperatures to a pure pink. At the same time, as has been observed before, the solubility of the substance in sulphuric acid is greatly diminished. A part always obstinately refuses to dissolve, even after long and repeated boiling with the concentrated acid, although this part is diminished by each successive treatment and appears to be in no way different from the rest of the substance. No difference, however, occurs in the readiness with which chlorine attacks it when intimately mixed with carbon. The formation of the chloride by this method is the easiest way of dissolving ignited thoria.

Two quantities of the same de-emanated thoria were converted, the one into chloride and the other into sulphate, by the usual methods, and from each of these the oxalate was formed by precipitation of the acid solution with oxalic acid. Parts of the oxalates were then converted into oxides by heating over the Bunsen burner. In both cases there was a very marked recovery in emanating

power; the oxide obtained from the sulphate had about 40 per cent, that from the chloride about 55 per cent, whereas the de-emanated thorium from which they were both produced had about 13 to 14 per cent of the emanating power of thorium. The oxalates from which the oxides were formed each had about 11 per cent of the power, and in converting them into oxides it was ascertained by a direct trial that too high a temperature had been employed and the thorium oxide had suffered partial de-emanation. At this time also, it was beginning to be realised that the emanating power was a quantity which varied, not only with the nature of the chemical compound, but also for the same compound very materially with its previous history. Thus the oxide from the oxalate does not possess as a rule so great an emanating power as that used for comparison, which would account for the above result. The following two exactly parallel experiments were therefore made—the one with ordinary, and the other with de-emanated thorium possessing 9 to 10 per cent of the emanating power of the first. Each was converted to chloride in the ordinary way, by mixing with sugar solution, carbonising, and igniting the mixture of oxide and carbon so obtained in a current of dry chlorine. Each sample was then treated with water, the thorium precipitated as hydroxide with ammonia, and the hydroxides washed and dried at 110°. The hydroxide prepared from the de-emanated thorium possessed 128 per cent, that from the ordinary thorium 108 per cent of the emanating power of ordinary thorium, when tested immediately after drying. Now a sample of hydroxide previously obtained had shown no less than three times the emanating power of ordinary thorium. The specimens were therefore tested again after having been kept for four days in loosely corked tubes. They now showed 157 per cent and 139 per cent respectively. The emanating power was thus increasing, so both specimens were exposed side by side in open watch-glasses under a sheet of glass to keep off the dust. The result is again conclusive:—

	From de-emanated ThO ₂ .	From ordinary ThO ₂ .
	Per cent.	Per cent.
After nine days	253	253
After three more days ..	259	259

Thus the process of de-emanating thorium by ignition does not irretrievably destroy the emanating power, for after solution and re-precipitation no difference whatever exists in the emanating power between ordinary and de-emanated thorium.

The results also bring out another point,—the marked effect of time and exposure to air in increasing the emanating power of thorium hydroxide. This will be examined more fully later.

A fair conclusion from these experiments is that the cause of the emanating power is not removed by ignition, but only rendered for the time being inoperative.

Radio-activity of De-emanated Thorium.—The "straight line" radiation of thorium, de-emanated as completely as possible by ignition, was compared with that of ordinary thorium oxide by the method described. It was found that within the limits of error no difference whatever could be detected between them. This result serves to bring out the fact that the power of thorium to give an emanation is independent of its power to give a direct radiation.

Is the Emanating Power a Specific Property of Thorium?

Having shown that the de-emanation of thorium by the processes described consists rather in a temporary obliteration of the effect than in a removal of the cause producing it, the next question to be considered is whether it is possible to remove from thorium compounds by chemical methods any constituent to which the property of emanating power can be traced.

The thorium used in the investigation is that supplied by

Messrs. Eimer and Amend, of New York, and is obtained from monazite sand by a secret process. It, of course, does not consist of pure thorium, although from superficial investigation it appears to be of excellent quality. There is a small quantity of a substance present which can be precipitated by sodium phosphate after removal of the thorium as hydroxide by ammonia, the nature of which is at present under investigation. The most noticeable impurity is about 1 per cent of thorium sulphate. Careful washing completely removed this impurity, and the emanating power of the washed sample was identical with the ordinary. The impurity may therefore be disregarded for present purposes.

Emanating power is not confined to thorium from any particular source. Orangeite and thorite from Norway both possess it, as well as monazite sand from Brazil. A specimen of thorium prepared from orangeite by the ordinary processes possessed about the same emanating power as that obtained from monazite sand by the secret process.

A quantity of thorium oxide was converted into the anhydrous sulphate and dissolved in ice water. The temperature was allowed to rise, and the hydrated sulphate precipitated in four fractions, a fifth being obtained by evaporation of the mother-liquor to dryness. These showed no marked difference in emanating power among themselves. The first fraction was dehydrated and again submitted to fractional precipitation as hydrated sulphate. The first fraction of the new series—designated fraction AA—was then compared in the following manner with the mother-liquor fraction of the first series—designated as fraction E. Both were dehydrated, dissolved in water, and precipitated as hydroxide by ammonia, washed and dried under the same conditions, and compared together at regular intervals with a comparison sample of ordinary thorium.

	Fraction AA. Per cent.	Fraction E. Per cent.
At first	203	200
After one day	240	249
After thirteen days	316	321
After forty-three days	352	372

The differences are too small to afford any indication of separation of the emanating material.

The straight line radiations of the two fractions tested in the apparatus (Fig. 2) also proved to be identical.

It was obviously useless trying any further fractionations by this method. Since there was no appreciable difference in either property in the fractions tried, there was nothing to be gained in a further repetition. These results completely accord with those of Sir William Crookes (*loc. cit.*), with which, however, we were not acquainted until after our own experiments had been performed.

Another method for the purification of thorium, employed by Dennis (*Fourn. Am. Chem. Soc.*, 1896, xviii., 947), the precipitation of the hydroxide by potassium azoisimide, was next tried. The latter reagent was prepared by Thiele's method (*Annalen*, 1892, cclxx., 1) from diazo-guanidine nitrate. Hydrazoic acid partially neutralised with potash precipitates thorium hydroxide from the boiling solution of a thorium salt. This hydroxide, compared with a sample which had been precipitated with ammonia in the ordinary way, showed similar emanating power.

These results, which fail to give any indication of a separation of the emanating material by chemical means, taken in conjunction with those already described in the preceding section on the regeneration of the emanating power in de-emanated thorium, certainly seemed to point to the conclusion that the power of giving an emanation is really a specific property of thorium. Recent results, which will be given in the last section, put the question in a fresh light.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, May 28th, 1902.

Prof. MELDOLA, F.R.S., Vice-President, in the Chair.

MESSRS. J. W. Peck, J. C. Crocker, and J. Kewley were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edwin T. H. Bucknell, Ebley House, Parsonage Street, Dursley, Gloucs.; Francis E. Francis, 8, Manilla Road, Clifton, Bristol; George Paton Pollitt, Ph.D., St. Silas Road, Blackburn, Lancs.; Harold James Roast, 3, Manor Park Road, Harlesden, N.W.; Edward J. Wheeler, Albany, State of New York, U.S.A.

Of the following papers, those marked * were read:—

*81. "Taxine, the Alkaloid of Yew." By T. E. THORPE, C.B., F.R.S., and G. STUBBS.

The investigation has been carried out on autumn-gathered leaves of male and female trees of the species *Taxus Baccata*. The alkaloid was extracted by digesting the powdered, air-dried leaves with 1 per cent sulphuric acid for five or six days. The acid liquid was strained and pressed from the leaves, and at once, without concentration, rendered alkaline, and extracted with ether. Taxine was obtained in the form of very fine, glistening particles, by crushing down the residue from the ether extract. It gives precipitates with most of the alkaloidal reagents, and colour reactions with strong sulphuric acid alone, and when this reagent is mixed with nitric acid, molybdic acid, or chromic acid.

Taxine is very susceptible to change. At least two substances result from the action of dilute acids upon it, but owing to lack of material the authors have not yet completed their investigation of these products.

Several salts have been prepared and analysed. Two compounds with gold chloride have been obtained which have the formulæ $C_{37}H_{52}NO_{10}, HAuCl_4$ (m. p. 72.5°) and $C_{37}H_{52}NO_{10}, AuCl_3$ (m. p. $132-134^\circ$) respectively. The methyl iodide compound, $C_{37}H_{52}NO_{10}, CH_3I$ (m. p. 121°), has been prepared as a white, amorphous powder by mixing benzene solutions of the alkaloid and methyl iodide.

Although the analytical figures deduced, both for taxine and its salts, are in substantial agreement with the formula, $C_{37}H_{52}NO_{10}$, given by Hilger and Brande (*Ber.*, 1890, xxiii., 464), the authors are not of opinion that this formula is definitely established.

The alcoholic extract of yew, amounting to about 26 per cent of the dry leaves, is at present under examination.

DISCUSSION.

Prof. DUNSTAN remarked that the authors had confirmed the accuracy of previous work on the properties of taxine, and he hoped that they would now be able to go further and throw some light on its chemical structure. It had not been yet fully proved that yew-poisoning was due to the presence of taxine, and indeed even the exact conditions under which yew becomes poisonous did not appear to have been determined with certainty.

Mr. GOLDING said that in the year 1893 he had assisted Mr. Dymond in an investigation of the alkaloid of the yew. They found that drying the leaves at 100° destroyed the alkaloid.

The extraction of the alkaloid was made from bruised, green, freshly-gathered leaves by Marmé's process, which was repeated several times to purify the alkaloid. Further purification was effected by adding light petroleum to the ether solution, the fractions thus obtained giving the characteristic reactions of taxine.

When dry hydrogen chloride was passed into a solution of the alkaloid in anhydrous ether, and a crystalline precipitate was formed, which soon changed to a dark brown paste, phenomena also observed by Hilger and Brande.

Cases were on record of animals eating yew with impunity, and a large number of the cases which had proved fatal were due to the eating of withered branches.

Dr. VOELCKER pointed out that the uncertainty with regard to poisoning by yew extended to the kind of animal eating it as well as the condition of the leaves. A good deal also depended on the conditions under which it was eaten; whether, for example, much grass or other food was eaten along with it. He thought that it was very desirable that the other substances which the authors had obtained should also be studied, but regarded it as essential that the yew examined should be freshly gathered, and not kept for some considerable time as in the case of that employed by the authors.

Mr. STUBBS, in reply, said that no work had been done to ascertain if the alkaloid contained methyl groups. He did not think that the substance had been produced by the action of the acid used for extraction upon a glucoside. The material employed had been dried in air, at a temperature not exceeding 60° . They had obtained the same amounts of alkaloid from the leaves both when freshly gathered and after they had been dried.

*82. "The Sampling of Soils." By J. W. LEATHER.

Experiments were made in India to determine the accuracy of the auger method of sampling soils, and the agreement between the samples was tested by determinations of the total nitrogen, the available phosphoric acid, and the available potash. The results showed that in most cases the agreement was very good between samples, but that in some cases the divergence exceeded 1 in 20, an amount which the author considered too great.

The amounts of phosphoric acid in some of the Rothamsted wheat soils, as found by Dyer, were considered with a view to determine the accuracy of the method of sampling which was there employed. The author considered that such a comparison indicated the Rothamsted method to have yielded as good results as the auger method. Both, however, fall short of what is expected in taking samples of commercial products, and it was urged that the newer methods of soil investigation demand more accurate methods of sampling.

DISCUSSION.

Dr. DYER said that it seemed obvious that a sample drawn from many parts of the field was more likely to be accurately representative than a sample drawn from one or few places. Nevertheless, it seemed to him that Dr. Leather's analytical results, obtained on samples drawn from different parts of the same field, instead of indicating differences in the samples, appeared really to indicate that both the sampling and the analytical work were excellently performed. Some of the analytical figures regarded by Dr. Leather as discrepant, he (the speaker) should himself regard as being in very good agreement. As to the results of his determinations of phosphoric acid in the Rothamsted wheat soils, which Dr. Leather had quoted, it must be remembered that, whilst the samples analysed represented only the first nine inches of soil, the phosphoric acid removed in the crops might in the case of wheat, on many plots, be drawn to a considerable extent from the subsoil; and that the influences of vegetation might considerably affect the distribution of soil constituents in the various layers of the soil and subsoil. The "original" phosphoric acid of Broadbalk field, as calculated back from the present contents, and known additions and removals, showed, on the whole, as Dr. Leather had pointed out, a fair uniformity, though there were some discrepancies. It was, however, quite probable that the percentage of phosphoric acid in the surface soil was originally by no means uniform on the different plots. Certain of the plots had long behaved somewhat anomalously, indicating some inherent physical or chemical differences in the soil or subsoil.

Dr. VOELCKER was inclined to agree with Dr. Dyer, and to regard the results which Dr. Leather had obtained as being very satisfactory, and as agreeing well with one another. It would hardly be a matter for surprise to those

who had followed the work at Rothamsted, and who knew the infinite pains which the late Sir Henry Gilbert always took to ensure accuracy in every detail, to learn that Dr. Leather's estimate of gains and losses showed that there could not be much amiss with the Rothamsted method of soil-sampling. Still, it was obvious that the more places in which borings of a soil were taken for sampling purposes the more representative would that sample be.

There was considerable difference between soil samples taken as at Rothamsted (where at least three holes were selected on each plot), and the block of soil ordinarily sent by a farmer when he wished his soil analysed. In the latter case, no doubt, the method Dr. Leather suggested would give a much more representative sample.

The difficulty was in the case of soils of stony character, or where lumps of chalk occurred. The auger might very readily, by pushing these stones or lumps aside, or by including them in the boring, ultimately cause a considerable difference in the analysis.

Mr. HALL said that for some years he had been using an auger for taking samples in the Soil Survey of Kent and Surrey they were carrying out. They used a cylindrical auger one foot long, two inches in diameter, with a slot one inch in breadth, the sides of the slot and the bottom of the cylinder being each sharpened to a cutting edge. The worm auger was only used for exploring the subsoil to some depth. The auger was undoubtedly most useful for securing a fair sample, especially in field work, where one did not want to be burdened with a great weight of soil; but there were many soils on which it could not be used, they were either too hard, too stony, or too loose to remain in the tool. The steel box employed at Rothamsted could be made to give the most accurate results, but it was not wise to lay down any hard and fast rule as to which was the best tool. The analyst must examine the soil, and then use his judgment.

As to Dr. Leather's figures, not only did they support his opinion that fair samples could be drawn with the auger, but they showed that he must have been working with an extremely uniform soil, probably of alluvial origin. In England samples taken from adjoining fields on the same formation would vary between far wider limits than those shown by Dr. Leather's figures.

Dr. LEATHER, in reply, said that so far as stones are concerned, the determination of their amount would naturally demand that comparatively large portions of soil should be taken, but this consideration would not apply to the examination of the fine earth. Of the Indian soils examined, that at Cawnpore is alluvial, but the geological history of the Poona land is uncertain.

*83. "Some Excessively Saline Indian Well-waters." By J. W. LEATHER.

The composition of some well-waters from the Muttra District, United Provinces, India, was given in detail. These waters contain from 200 to 2000 parts of salt per 100,000 of water. About one-half of the saline matter consists of sodium chloride; the amount of carbonate is about 20 to 30 parts; the nitrate varies from nothing to 250 parts; very large amounts of sulphate were present in some of the samples. In three cases, there was an excess of lime over that required to combine with the nitric, carbonic, and sulphuric acids, thus proving the presence of calcium chloride.

Some of these waters are used for irrigating crops. The soil of the district is open, the drainage conditions are good, and no salts accumulate in the surface soil. These waters provide an indication therefore of the maximum strength of solutions in which plants can grow, a point which is of importance in connection with the alkali lands of America and the Usar lands of India. It is found practically that, of these well-waters, those may be employed for irrigating crops which do not contain much more than about 500 parts of salts per 100,000, or 0.5 per cent.

The amount of salts in Usar or alkali land is usually stated in parts in 100 of soil, and it is found in practice

that soils containing much more than 0.1 per cent are infertile. Immediately after irrigation, such a soil would contain a solution of about 0.33 of salts per 100 of water, but after the lapse of a few days, the proportion of water decreases to 10 or 15 per cent, and in this state the above mentioned solution would become concentrated to about 1.0 or 0.66 per cent respectively. These figures correspond practically with what is known about the well-waters.

DISCUSSION.

Mr. J. SPILLER said that in the year 1865 he had occasion to examine some remarkable products obtained from a highly saline spring which discharged itself into Lake Lohhar, India. The water left on evaporation 8.25 per cent of solid residue, which consisted roughly of two parts of common salt to one of sodium carbonate. A local attempt at a separation of these resulted in a purified product, which had the following composition:—

Sodium carbonate	75.0
chloride	0.6
Calcium carbonate	1.9
Sand and ferric oxide	2.7
Water, nearly	20.0

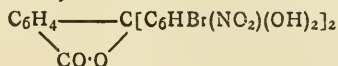
There was no sulphate, bromide, borate, or nitrate.

*84. "Nitrobromo-derivatives of Fluorescein." By J. T. HEWITT and A. W. G. WOODFORD.

The non-fluorescence of alkaline solutions of nitro-derivatives of fluorescein was explained by the assumption that the alkaline salts of orthonitrophenols have the metal attached to the nitroxyl and not to the hydroxyl group (Hewitt and Perkins, *Trans.*, 1900, lxxvii., 1324). With regard to the position of the nitro-groups in dinitrofluorescein, it was assumed that these occupied positions 2 and 7. (The numbering of the fluoran ring corresponds to Richter's numbering in the xanthene nucleus).

Additional support was lent to this view by the isolation from the product of alkaline fusion of a small amount of material having a melting-point of 114°. Since 4-nitroresorcin melts at 115°, the substances were supposed to be identical, and hence positions 2 and 7 were assigned to the nitro-groups in the fluoran nucleus. It is now shown, however, that this view must be discarded; by adopting suitable precautions, 2-nitroresorcin may be isolated in considerable quantity, as had been previously demonstrated by Matras; the authors' thanks are due to M. Reverdin, of Geneva, for calling their attention to this work.

Dinitrofluorescein is thus 4:5-dinitrofluorescein; acted on by bromine, 4:5-dinitro-2:7-dibromofluorescein results. This substance closely resembles the original dinitrofluorescein; it dissolves in alkalis with a brown colour, but on warming a blue solution is obtained from which acids precipitate the hydrate—



4:5-Dinitro-2:7-dibromofluorescein has been further characterised by its *diacetyl* derivative, $\text{C}_{20}\text{H}_6\text{Br}_2\text{N}_2\text{O}_9(\text{C}_2\text{H}_3\text{O})_2$, m. p. 276°; *dibenzoyl* derivative $\text{C}_{20}\text{H}_6\text{Br}_2\text{N}_2\text{O}_9(\text{C}_7\text{H}_5\text{O})_2$, m. p. 315°; *sodium salt*, $\text{C}_{20}\text{H}_6\text{Br}_2\text{N}_2\text{O}_9\text{Na}_2 \cdot 2\text{H}_2\text{O}$.

Dibromofluorescein, $\text{C}_{20}\text{H}_{10}\text{Br}_2\text{O}_5$, obtained by Bayer by the limited action of bromine on fluorescein, is evidently also a 4:5-substitution derivative, since nitric acid produces from it a dinitro-derivative quite distinct from the 4:5-dinitro-2:7-dibromo-compound. The *benzoyl* derivative, $\text{C}_{20}\text{H}_8\text{Br}_2\text{O}_5(\text{C}_7\text{H}_5\text{O})_2$, melts at 240–244°. 2:7-Dinitro-4:5-dibromofluorescein may be obtained either by the action of nitric acid upon 2:7-dibromofluorescein or of bromine upon 2:4:5:7-tetranitrofluorescein. This substance dissolves in alkalis with a magnificent purple colour not altered by boiling. Nitro-groups only render the pyrone ring unstable if in the ortho-position relatively to its oxygen atom; this is also shown by the action of ammonia, which reacts with 4:5-dinitro-2:7-dibromofluorescein, apparently in a similar manner to that ob-

served by Reverdin in the case of dinitrofluorescein, whilst with 2:7-dinitro-4:5-dibromofluorescein it merely produces an ammonium salt.

The diacetyl derivative, m. p. 215° ; dibenzoyl derivative, m. p. 301° ; and sodium salt of 2:7-dinitro-4:5-dibromofluorescein have been prepared.

(To be continued).

THE ROYAL SOCIETY.

CONVERSAZIONE AT BURLINGTON HOUSE.

A VERY well attended and successful *Conversazione*, to which ladies were also invited, was held at the Society's Rooms, Burlington House, on Wednesday evening last, June 18th. The Fellows and guests were received by Sir William and Lady Huggins, and many distinguished visitors were present.

Among the interesting and varied exhibits we may mention an Apparatus for Liquefying Hydrogen, exhibited by Dr. MORRIS TRAVERS. Hydrogen, when compressed at the ordinary temperature and allowed to expand, becomes warmer, while air under the same conditions becomes colder; at temperatures below -80°C ., hydrogen becomes an imperfect gas, in the same sense as air, and undergoes cooling on free expansion (Joule-Kelvin effect). The gas, under a pressure of 120–150 atmospheres, passes through coils in the interior of the apparatus; these coils are cooled in solid carbonic acid and alcohol (-78.5°C .), in liquid air (-185°C .), and in liquid air boiling under reduced pressure (-200°C .). It then enters a regenerator coil, and expanding at a valve at the bottom is partially liquefied. The liquid collects in a vacuum-vessel at the bottom of the apparatus; the unliquefied gas passes upwards through the regenerator coil, cooling the gas it contains, and returns to the compressor.

Prof. W. RAMSAY showed an attempt to reproduce an Aurora Borealis. The spectrum of the aurora borealis has been shown to contain lines due to the presence of krypton; the great majority of the lines, if not all, are coincident with those of the krypton spark spectrum. An electrode-less discharge in air gives a spectrum in which the leading green line of krypton, 5570.5 , is distinctly visible at low pressures. This discharge can be deflected by a magnet, sending out streamers in the lines of magnetic force. The main phenomena of the aurora are thus reproduced.

Prof. H. L. CALLENDAR showed an Apparatus for Determining the Mechanical Equivalent of Heat, by which measurements of one part in a thousand can be obtained; he also showed some vacuum-jacket calorimeters embodying the most recent improvements.

The West Indian Volcanoes Committee showed some specimens and photographs illustrating the fall of volcanic dust at Barbados on May 7th and 8th, 1902; while Mr. HENRY CROOKES also showed specimens and photographs of a similar nature, viz.:—

(1). Volcanic Dust from La Soufrière, St. Vincent. This dust erupted from La Soufrière, and fell upon Barbados, May 8th, 1902. It is estimated that from 2,000,000 to 3,000,000 tons fell in seven or eight hours.

(2). Volcanic Dust collected from the steps at Roxborough, Grenada, about 90 miles from La Soufrière, May 8th, 1902.

(3). Volcanic Dust from the explosion of Mont Pelée, Martinique. This specimen is of special interest, as it was collected on the deck of the S.S. *Roddam*, Captain Freeman, on her arrival at St. Lucia. The *Roddam* was the only ship that escaped from St. Pierre, and many of her crew were burned to death.

(4). Micro-photographs of the above specimens of volcanic dust.

(5). Microscopic Slides of the same viewed with ordinary, and with polarised light.

(6). Scoria, from the eruption at Krakatoa in 1883, taken from the sea about 400 miles from the volcano.

The microscopic examination of the dust from the deck of the *Roddam* shows that it consists of nearly equal amounts of mineral and rock fragments, from about one five-thousandth to one-hundredth of an inch in diameter, but commonly seven- or eight-thousandths of an inch. The minerals are felspar (generally labradorite), augite, and hypersthene; the rock fragments, a pale brownish-grey scoria, in one or two cases red, generally opaque, and with traces of a brown glass. The dust from La Soufrière from Barbados is of a very similar character, each representing a rock of the same species, viz., that called "Hypersthene-andesite."

Dr. G. JOHNSTONE STONEY showed some Experiments Exhibiting Interference between Portions of Light from Independent Sources. In one experiment a spectrometer is employed, in the other a microscope. In both, spectra will be seen. These are produced because interference directs the light with different intensities towards the various directions; and in the present experiments, essential interfering portions of the light are taken from widely separated parts of a flame, and therefore come from independent sources.

During the evening demonstrations by means of the electric lantern were given in the Meeting Room by Prof. W. M. FLINDERS PETRIE on Early Civilisation in Egypt; by Mr. J. Y. BUCHANAN, who showed a series of Lantern Slides, illustrating the performance of M. Santos Dumont's dirigible balloon and the accident to it on February 14th, 1902; and by Prof. E. B. POULTON, on Recent work upon Protective Resemblance and Mimicry in Insects, illustrated by three-colour slides.

PHYSICAL SOCIETY.

Ordinary Meeting, June 13th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

THE meeting was held in the National Physical Laboratory by the kind invitation of the Director.

Dr. GLAZEBROOK made a brief statement, and said that the task of fitting up an ordinary house as a physical laboratory had been a difficult one, much more difficult than that of designing a new building. The general scheme of the laboratory is such that the main departments, including those of electricity, thermometry, and chemistry, occupy the principal rooms in four of the wings, together with the portions of the basement most nearly adjoining, while the first floor and a number of small rooms are fitted up as general laboratories. An additional building has been constructed for carrying on the work of the engineering department. Electric current is supplied by fifty storage-cells and distributed by bare wires carried by porcelain insulators. From the main switchboard and four subsidiary switchboards, circuits are led to almost every room in the building, and to these any voltage from 2 to 110 can be applied by making a suitable connection.

The meeting then adjourned, and the Fellows were allowed to inspect the laboratory.

Thermometry.—Dr. HARKER showed apparatus for testing thermometers at high and low temperatures, including:—

- (i.). An oil-bath. Temperatures 100°C . to 240°C .
- (ii.). A bath of fused nitrates of sodium and potassium. Temperatures 240°C . to 550°C .
- (iii.). Electric ovens. Temperatures up to 1250°C .
- (iv.). A vacuum vessel with suitable cooling agents.

High-temperature mercury thermometers, platinum thermometers, and thermopiles were shown in operation, and a demonstration was given with the Hampson apparatus for the liquefaction of air.

Electricity.—Mr. CAMPBELL and Mr. MELSOME showed:

- (i.). A Kelvin electrostatic voltmeter with a long scale and arrangements for calibrating against a Clarke's cell.
- (ii.). A Kelvin current-balance,

- (iii.). Apparatus for determining the capacity of the standard air-condensers of the British Association.
- (iv.). Apparatus for tests on iron by the ballistic method.
- (v.). Ewing's permeameter.
- (vi.). Bridge for resistance measurements.
- (vii.). Methods for measuring a small resistance:—
 - (a) Thomson's double bridge.
 - (b) Potentiometer method.
 - (c) Differential galvanometer method as described by Crawley.

Electrical Standards.—Mr. SMITH showed the British Association standards of resistance, and the standard cells in a room maintained at a constant temperature by a gas-fire and a regulator.

Terrestrial Magnetism.—The latest form of unifilar magnetometer, designed for the Indian Survey, together with some recent magnetic and seismographical charts were shown by Dr. CHREE. Mr. Watson's magnetographs, arranged for the special magnetic observations in connection with the Antarctic Expedition, were exhibited.

Microphotography.—Dr. CARPENTER exhibited the Zeiss microphotographic outfit, and showed some microphotographs of steel.

Metrology.—The following apparatus was shown by Mr. KEELING:—

- (i.). A Whitworth measuring machine.
- (ii.). A Pratt and Whitney measuring machine.
- (iii.). A dividing engine by the Société Genevoise.
- (iv.). A simple comparator.
- (v.). A comparator by the Société Genevoise.

Photographic Lens-testing.—Mr. HUGO exhibited the Kew apparatus for testing photographic lenses.

The chemical laboratory, the metallurgical laboratory, and the main switchboard room were also open for inspection.

In the *Engineering Laboratory* Dr. STANTON and Mr. JAKEMANN showed the steam turbine and dynamos, the gauge-testing apparatus, the experimental testing machine, and the other machines which have been installed.

NOTICES OF BOOKS.

Grundriss der Qualitativen Analyse. By Dr. WILH. BÖTTGER. Leipzig: Wilhelm Engelmann. 1902.

THE rapid spread of the ionic theory, in spite of many opponents, creates a demand for text-books written in accordance with new ideas, and adapted for students' use, and there seems to be no fear but that this want will be amply supplied. This book gives a thoroughly satisfactory introduction to the study of qualitative analysis from the ionic point of view, and will prove specially useful to those who are using Ostwald's "Grundlinien der Anorganischen Chemie," to which references are constantly made. Innovations in matters of detail are not wanting, but will in nearly all cases justify themselves; such theoretical discussions as are introduced are carefully worded, though perhaps occasionally the student may find them a little above him. The reactions of kations occupy the first part of the book; here the ordinary order of procedure is reversed, and the student studies first the separation of the metals of a group, and then passes on to the examination of the characteristic reactions of each metal. It is doubtful whether this plan is an improvement on the more usual one of deducing as far as possible the method of separation from the previously observed reactions of the different individual members of a group; however, it would be easy for the teacher to modify this arrangement at his discretion. The anions are grouped more systematically than is usually the case, and if Dr. Böttger's method is strictly observed no difficulty should be found in the detection of acid radicles. The book concludes with directions for the detection of the rarer elements.

Die Elektrolyse des Wassers. By VIKTOR ENGELHARDT. Halle-a-S.: Wilhelm Knapp. 1902.

THIS volume is the first of a series of monographs on applied electrochemistry, to be issued quarterly. The aim of the authors of these monographs is to be the production of complete and trustworthy accounts of special branches of the rapidly developing science of electrochemistry; each volume will treat of the historical development of its special subject, and will endeavour to give a good insight into the most recent advances relating to it, and the hope is expressed that both the practical man and the student may derive instruction from them. This first volume deals with the electrolysis of water. Distinction is made between those methods and apparatus suitable for laboratory work and the lecture table, and those better adapted for use technically on the large scale. Patent specifications have been carefully searched, and are freely quoted and summarised, and useful commercial data, such as the cost of building the plant and carrying on the processes, are given in considerable detail. The issue of future volumes on such subjects as the electrometallurgy of iron, the preparation of ozone, and the electrolysis of organic compounds will be awaited with interest.

Catalogue of the Educational Collection of Minerals Belonging to the West Ham Municipal Technical Institute. Compiled by H. A. AUDEN, D.Sc., M.Sc., Head of the Chemical Department.

THIS catalogue has been compiled with a view to illustrate the systematic grouping of mineral specimens.

Each opening of the catalogue is divided into ten columns, giving the specimen number, name and composition, system, synonyms and varieties, isomorphic grouping, &c., colour, similar minerals, associated minerals, hardness, and specific gravity.

The classification adopted is based on that of Klockmann, and is clear, comprehensive, and systematic.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 21, May 26, 1902.

Synthesis of certain Petrols. Theory of Formation of Natural Petrols.—Paul Sabatier and J. B. Senderens.

—The author succeeds in synthesising several petrols, and deduces from this a very simple explanation of the formation of natural petrols. In the depths of the earth the alkaline and alkaline earth metals in the free state are widely distributed besides their carbides. Water on coming in contact with these metals causes the evolution of hydrogen, whilst, in contact with the carbides, acetylene is evolved. These two gases in variable proportions come in contact with the various metals found in nature (nickel, cobalt, iron, &c.) in a finely divided state, and certain reactions occur by which the various petrols are furnished.

Certain Physical Properties of Hydrogen Telluride.—MM. de Forcrand and Fonze-Diacon.—The authors prepare pure hydrogen telluride and determine the following constants:—

T (temperature of ebullition), 0° C. or 273° abs.

T' (temperature of fusion), -48° C. or 225° abs.

D (liquid density), 2.57.

PM/D (molecular volume), 49.75.

In the case of H₂S and H₂Se the constants are as follows:—

	H ₂ S.	H ₂ Se.
T	211.4°	231°
T'	187°	209°
D	0.86	2.12
PM/D	39.53	38.20

The molecular volume differs considerably from the almost identical values found for the other two gases, and still more from that of water (18.82).

Preparation and Properties of Chloro-, Bromo-, and Iodo-sulphobismuthites of Copper.—Fernand Ducatte.—The presence of a halogen element in definite proportion which the author has found in the products resulting from the action of lead chloride, bromide, or iodide on bismuth sulphide, Bi₂S₃, is not an isolated fact, but products are obtained analogous with cuprous chloride, bromide, and iodide, and bismuth sulphide. The proportion of the halogen is determined by the formula 2Cu₂S.Bi₂S₃.2BiSX, in which X can be replaced by Cl, Br, or I.

The Alkaline Cobaltioxalates.—M. Copaux.—Of the three alkaline cobaltioxalates which are known up to the present time only one has had a definite formula attributed to it:—Co₂(C₂O₄)₆(NH₄)₆.6H₂O. The ammonium, potassium, and rubidium salts of this series are isomorphous amongst themselves. The iron, aluminium, and chromium salts differ in form and in composition. This fact, singular in itself, shows that cobalt possesses a specific property. If the double salt of the sesquioxides (of which a table is given in this paper) are specially examined, it is seen that cobalt takes up a position further from iron and nearer to chromium and aluminium.

Constitution of Ammoniacal Cupric Salts. Action of Ammonia.—M. Bouzat.—The author examines the ammoniacal compounds of copper with a view to establishing their composition, and his experiments show that the following law is true: the quantity of heat evolved during the combination of ammonia with a cupric salt derived from a strong acid is the same whichever cupric salt is used. This law can be extended to zinc and all the metals which give with ammonia compounds analogous to ammoniacal copper salts. This law shows that the ammoniacal copper compounds ought to be considered as salts of complex bases.

***p-p*-Dinitrohydrazobenzene.**—P. Freundler and L. Béranger.—The nitration of diacetylhydrazobenzene gives as principal product a nitrated derivative, NO₂.C₆H₄.N(CO.CH₃)N(CO.CH₃).C₆H₄.NO₂, which crystallises from acetone in yellowish plates, fusing at 186–187°. These are very slightly soluble in alcohol and ether. At the same time a small quantity of *p-p*-dinitroazobenzene is obtained, fusing at 220°. The authors examine the constitution of this di-nitrated derivative by transforming it into dinitrohydrazobenzene by means of saponification, and they find it to possess the formula HO.ON=C₆H₄=N=N=C₆H₄=NO.OH.

Thiosulpho-carbamic Ether Derivatives of Primary Amines.—Marcel Delépine.—Dithiourethanes of general formula R.NH.CS.SR' Hofmann has shown can be obtained by condensing the sulpho-carbimides with the mercaptans R.N:C:S+H.SR'=R.NH.CS.SR'. This reaction has the inconvenience of necessitating the preparation of two constituents with a very unpleasant smell. The author finds that the dithiourethanes of the above type can be easily obtained by the action of a single molecule of a halogen ether on the sulphocarbonic compounds of primary amines; that is to say, by stopping the reaction at the first phase of the preparation of the imido-dithiocarbonic ethers, the reaction taking place according to the equation NHR.CS.S.NH₃R+XR'=RNH.CS.SR'+X.NH₃R.

Synthesis of Aldehydes of the Fatty Series by means of Nitromethane.—L. Bouveault and A. Wahl.—The authors succeed in transforming a fatty aldehyde into its superior homologue, in the same manner as in the aromatic series, owing to the action of nitromethane.

In the first case they employ isovaleric aldehyde and cenanthol.

Mechanism of Chemical Reactions taking place in Plants submitted to the Influence of Sodium Nitrate.—E. Charabot and A. Hébert.—In the same way as sodium chloride, sodium nitrate has the effect of causing etherification in plants and accentuating the diminution of the percentage of water. These two salts modify in an analogous manner the series of chemical phenomena in plants. The mechanism of their intervention, however, does not appear to be the same.

Composition and Volumetric Estimation of Sodium Methylarsinate.—MM. Adrian and Trillat.—To determine the composition of sodium methylarsinate or arrhenal, the authors successively estimate—(1) The quantity of pyroarsenate of sodium obtained by heating the substance with nitric acid and calcining the residue at a dull red heat; (2) the quantity of arsenic in the state of magnesium pyroarsenate; (3) the quantity of water of crystallisation. The true formula is thus proved to be CH₃AsO(NaO)₂+6H₂O. The volumetric estimation of this substance is based on the precipitation of sodium methylarsinate by a known solution of silver nitrate in excess; this excess being afterwards titrated, after filtration, against ammonium sulphocyanate.

MISCELLANEOUS.

Estimation of Copper in the State of Oxalate, and on a Method of Separating Copper from Cadmium, Arsenic, and Tin.—C. A. Peters.—In a solution of sulphate of copper of about 50 c.c. and containing not less than 0.0128 gm. of CuO, the copper can be completely precipitated in the form of oxalate by the addition of oxalic acid, especially in the presence of a moderate quantity of nitric acid (such as 5 c.c. of the concentrated acid). Under these conditions cadmium, arsenic, and iron, and even small quantities of tin (but not zinc) remain dissolved.—*Zeit. Anorg. Chem.*, vol. xxvi., p. 111.

Action of Zinc Powder on the Dibromides, C_nH_{2n}Br₂.—V. Ipatief.—Fresh experiments have shown that in the action of zinc powder and alcohol on the bromide, (CH₃)₂CBr—CH₂—CH₂Br, the carbide which is formed in the greatest quantity (about 30 per cent), is isopropylethylene, boiling at 21–22°. There is also formed a substance which distils over between wide limits, 80–130°, and contains about 8 per cent of bromine; this is a mixture of non-saturated ether, non-saturated bromide, and perhaps some oxide of dimethyltrimethylene-glycol. According to this, in the formation of the carbide by means of the bromide of α -dimethyltrimethylene, zinc powder, and alcohol, one molecule of HBr is removed at the expense of the Br united to the most hydrogenised C, and the Br united to the tertiary C is replaced by H.—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 647.

The Thiocyanates of Copper and Silver in Gravitric Analysis.—E. G. Van Name.—The estimation of copper in the state of cuprous thiocyanate has already been recommended by Rivot; the author has modified the method so far as concerns the collection of the precipitate. The cupric solution is first treated with bisulphite of sodium, then with an excess of sulphocyanate of ammonium. The precipitate of (CNS)₂Cu₂ is collected on a layer of asbestos in a pierced crucible of which the weight is known; it is then washed with cold water, dried at 110°, and weighed. The estimation of the silver is effected in almost the same manner, except that no bisulphite is used. The CNS.NH₄ should be free from chloride; and further, should not be used in excess, as it re-dissolves the precipitate.—*Zeit. Anorg. Chem.*, vol. xxvi., p. 230.

ERRATA.—The Papers by Mr. R. S. Hutton, B.Sc. (p. 159), and Mr. R. A. Taylor, F.C.S. (p. 269), were reprinted from the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*.

THE CHEMICAL NEWS.

Vol. LXXXV., No. 2222.

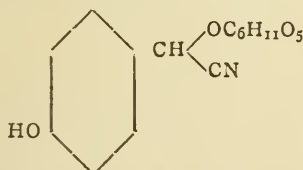
CYANOGENESIS IN PLANTS.*

PART II.—THE GREAT MILLET, *Sorghum vulgare*.†

By WYNDHAM R. DUNSTAN, M.A., F.R.S.,
Director of the Scientific Department of the Imperial Institute,
and
T. A. HENRY, D.Sc., Lond.

THE authors have investigated the nature of the poison contained in the young plants of *Sorghum vulgare*, the Great Millet or Guinea Corn (the *Yuár* of India or *Dhurra shirshabi* of Egypt). This plant is cultivated in tropical countries for the sake of the seed, which is important as a food grain. The young plants have proved fatal to animals, especially in Egypt, where the attention of the authors was directed to the subject by Mr. E. A. Floyer, of Cairo, who has kindly provided the material required for the investigation.

The authors show that the young plant, but not the seeds or old plants, when crushed with water furnishes prussic acid (about 0.2 per cent of the dried plant). The acid is not present in the free state, nor is it produced by acting on the plant with boiling water or with alcohol. The production of the poison is due to the action of a hydrolytic enzyme, apparently identical with the emulsin of bitter almonds on a cyanogenetic glucoside which has been named "dhuririn," from the Arabic name for the plant, "dhurra." This glucoside has been proved to be derived from parahydroxymandelic nitrile by the association of the residue of one molecule of dextrose. Its formula is therefore $C_{14}H_{17}O_7$,—



Dhuririn crystallises well, and is soluble in both water and alcohol. When hydrolysed by emulsin or by dilute acids it is converted into parahydroxybenzaldehyde, dextrose, and hydrocyanic acid according to the equation $C_{14}H_{17}O_7N + H_2O = C_7H_6O_2 + C_6H_{12}O_6 + HCN$. When warmed with alkalis, dhuririn is resolved first into dhurinic acid and ammonia. This acid subsequently undergoes further hydrolysis when warmed with dilute hydrochloric acid into parahydroxymandelic acid and dextrose (1) $C_{14}H_{17}O_7N + H_2O = C_{14}H_{18}O_9 + NH_3$, (2) $C_{14}H_{18}O_9 + H_2O = C_8H_8O_4 + C_6H_{12}O_6$.

The identity of the parahydroxymandelic acid was established by its synthesis from the cyanhydrin of parahydroxybenzaldehyde.

Dhuririn differs from the other two known cyanogenetic glucosides, the amygdalin of bitter almonds and the lotusin found by the authors in *Lotus arabicus*, in being derived from dextrose and not from maltose.

The authors point out the protective purpose served by the existence of the cyanogenetic glucoside in the young plant.

The authors intend to fully investigate the several problems which are raised by the occurrence of cyanogenetic glucosides in plants.

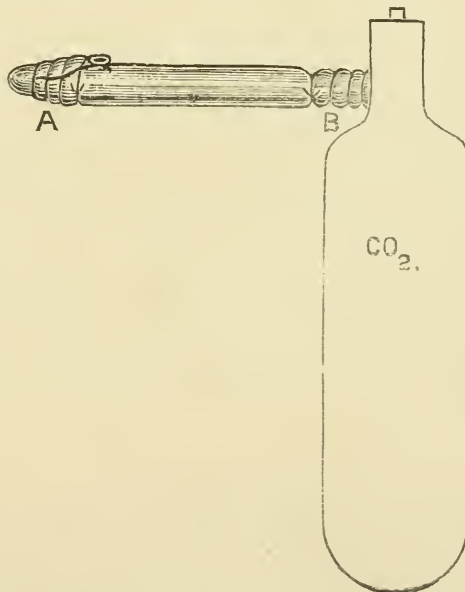
* Abstract of a Paper read before the Royal Society, May 15, 1902.
† The authors' previous paper, entitled "The Nature and Origin of the Poison of *Lotus arabicus*" (*Proc.*, 1900, vol. lxvii., p. 224; 1901, vol. lxviii., p. 374; and *Phil. Trans.*, B., 1901, cxvix., p. 515), is to be regarded as Part I. of this series.

They are at present engaged in examining several other plants which have furnished prussic acid, among them being *Manihot utilissima*, *Linum usitatissimum*, *Lotus australis*, and *Phaseolus lunatus*.

A SIMPLE METHOD OF COLLECTING SOLID CARBON DIOXIDE FOR LECTURE PURPOSES.

By CHAS. R. DARLING, A.R.C.Sc.(Ire.), A.I.C., F.C.S.

MOST lecturers must have experienced disappointment in attempting to collect solid carbon dioxide in quantity by means of the metallic box sold for the purpose. This arrangement is inefficient for two reasons; firstly, being made of thin metal and possessing a large surface, it affords every facility for the passage of heat from the atmosphere to the interior of the box; and secondly, the meshes placed in the handles are not sufficiently close to retain the particles of solid. Far better results are obtained by the method of tying a piece of flannel round the nozzle of the cylinder, although in this case also a large quantity of the solid escapes through the single layer of flannel.



The following method, which to the best of my knowledge has not previously been published, will be found to give excellent results:—A piece of coarse flannel (such as is used for floor-cloths), about 15 inches square, is rolled round a piece of rod or tubing $1\frac{1}{2}$ inches or more in diameter.

The rod is partially withdrawn, and one end of the flannel bent over on itself, and tied with string, as shown at A. The rod is then completely removed, and the other end of the flannel tube tied with string round the nozzle of the CO_2 cylinder, as at B. The gas is then turned on for a short time until the whole length of the flannel feels hard to the touch. On cutting the strings, and removing and unrolling the flannel, a solid rod of carbon dioxide, much denser and harder than that obtained by the usual methods, and about 8 inches long, will be found. This may be kept for a considerable time rolled up in the flannel, or may be transferred to a Dewar vacuum vessel, and used for several experiments.

I have used this method for some time for lecture purposes, and on occasions when a quantity of solid carbon dioxide has been required for cooling purposes, and have found it uniformly successful. There is no restriction as to the diameter of the rod round which the flannel is wound, providing the material is large enough to pass four or five times round the rod. The efficiency of the method is no doubt due to the retention of the finest particles of solid, owing to the several layers of flannel through which the gas must escape, and also to the heat-insulating properties of the material which serve to protect the solid from extraneous heat. The preparation of solid carbon dioxide by this method will be found to form a most striking lecture experiment.

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CONTRIBUTIONS TO THE CHEMISTRY OF THE RARE EARTHS OF THE YTTRIUM GROUP.*

I.

By L. M. DENNIS and BENTON DALES.

(Concluded from p. 293).

Treatment with Potassium Trinitride, KN₃.

THE method proposed by Dennis and Kortright (*Zeit. Anorg. Chem.*, vi., 35) for the separation of thorium from members of the cerium and yttrium groups, by means of potassium trinitride, was tried to see if perhaps some reaction similar to the one for thorium could be found. The results were entirely negative. Partial precipitation by potassium trinitride was found to fraction the rare earths of this group rather slowly. The precipitate in the case of thorium was thorium hydroxide. In this case it seemed rather to be a basic nitrate. It was white, very finely divided, and adhered to the beaker, and had also a tendency to go through the filter.

A dilute solution of the nitrate ($R^{III} = 112.16$) was treated with a dilute solution of potassium trinitride containing free hydronitric acid and boiled. A precipitate was obtained on boiling for two or three minutes. It was filtered, washed with hot water, dissolved in nitric acid, and converted into oxalates. The atomic weight was 118.96. The nitric acid solution was pink, and the absorption bands were practically the same as in the original solution.

Fractional Precipitation with Ammonia.

The work of many chemists who have investigated the earths of the yttrium group has shown that these elements can unquestionably be partially separated by a long series of fractions with dilute ammonium hydroxide, but the work is so extremely tedious and the separations are so very slow that it is questionable whether this procedure can be considered to be of material value. As an illustration of the slight effect of fractionation by this reagent one experiment will suffice.

A very dilute solution of the neutral chlorides containing about 57 grms. of the oxides in 12 litres was treated with an amount of dilute ammonia sufficient to precipitate only one-tenth of the earths present. During the addition of the ammonia the solution was vigorously stirred by blowing through it a blast of air, and this stirring was continued for about an hour. A precipitate formed very slowly. The hydroxides were then washed by decantation until the wash-water gave no precipitation with ammonia. The mother-liquor and wash-waters were evaporated to the original volume, and precipitated again with the same amount of ammonia. The atomic weights of the earths

precipitated in these two treatments were 103.9 and 104.0, while that of the original material was 96.

Fractionation with Ammonium Carbonate and Dilute Acetic Acid.

Mosander (*Phil. Mag.*, xxiii., 251; *Liebig's Ann. Chem.*, xviii., 219) in 1843 mentioned that the hydroxides of the rare earths of this group are soluble in a concentrated solution of ammonium carbonate, and that they could be fractionated in this way. Krüss also mentioned this solubility (*Liebig's Ann. Chem.*, cclxv., 1).

This treatment alone was first tried here. The results were much better than was expected. The rare earth hydroxides were precipitated by ammonia (the latter need not be washed out). By a single treatment of these hydroxides with a quantity of a saturated solution of ammonium carbonate sufficient to dissolve one-fourth of the whole, an earth mixture was dissolved whose metal atomic weight was 121.41. The bases in the undissolved portion had an atomic weight of 107.94, while the original solution contained a metal mixture of atomic weight 108.08.

Quantities of saturated ammonium carbonate solution sufficient to dissolve other amounts of the precipitated hydroxides than one-fourth were then tried on different portions of this earth-mixture. An amount of carbonate solution sufficient to dissolve one-tenth of the hydroxides precipitated was added to one portion, while to others were added amounts of the carbonate solution sufficient to dissolve nine-tenths, one-fifth, one-third, and one-half. On the whole, however, the addition of one-fourth or perhaps one-fifth the amount of carbonate solution necessary to dissolve all the hydroxides seems to be most suitable for this method of fractionation. The total precipitation of the earths by a solution of ammonium carbonate with partial solution of the precipitate in an excess of that reagent was also tried, but this is no better than precipitation with ammonia and partial solution in ammonium carbonate. A second extraction of the hydroxides from the undissolved portion ($R^{III} = 107.94$) from the first treatment was made, and the atomic weight of the metal mixture which dissolved was 125.91. Evidently the material could be thus extracted at least twice with profit.

To the dissolved portion mentioned above ($R^{III} = 121.41$) there was then added very dilute acetic acid (1:30) slowly and with constant stirring, first adding concentrated acetic acid just to turbidity. This treatment had a most marked effect. The granular precipitate thrown out was of a pink colour, and when dissolved showed all the absorption bands very strongly, while the bands in the remaining solution were much weakened.

When the dilute acetic acid had been added as above, a point was reached at which the addition of more acid would produce no further precipitate. This is due to the fact that the rare earth hydroxides of this group are nearly as soluble in ammonium acetate as in ammonium carbonate, and a state of equilibrium is soon reached between the three, after which dilute acetic acid has no effect upon the double ammonium salts of the rare earths. It was necessary, when this point was reached, to filter, decompose the ammonium carbonate solution with hydrochloric acid, dissolve the precipitate which was formed by further addition of the acid, and then to precipitate the whole with ammonia, wash, re-dissolve in hydrochloric acid, and re-precipitate with ammonia. The hydroxides were then dissolved in saturated ammonium carbonate solution, and the precipitation by dilute acetic acid repeated.

This particular material after having been treated three times with ammonium carbonate and dilute acetic acid in the manner above described, gave a very small amount (less than 1 gm.) of an earth which yielded a white oxalate and a white oxide. A determination, not in duplicate, of its metal atomic weight gave the interesting result of 170. In the dry oxide only, the green absorption band of erbium was visible by reflected light. In saturated solution this earth mixture did not show the absorption

* *Journal of the American Chemical Society*, vol. xxiv., No. 5.

bands of holmium, thulium, nor dysprosium, but those of erbium and samarium were visible. They were, however, much weaker than in the original solution. The spark spectrum of this solution was also examined, and the following lines of ytterbium as given by Thalén were found (*Journ. de Phys.*, [2], ii., 37):—

Angle.	Wave-length.	Thalén's measurements.
10° 57' 00"	6220·9	6221·0 (1)
0° 46' 00"	5555·6	5555·5 (1)
0° 37' 30"	5475·7	5476·0 (1)
0° 24' 30"	5353·5	5352·0 (1)
0° 22' 30"	5334·8	5334·0 (1)
0° 18' 50"	5300·3	5300·0 (4)
8° 24' 10"	4785·7	4785·5 (2)
8° 17' 40"	4724·5	4725·0 (2)

The spark spectra of erbium and samarium were very weak. None of the characteristic gadolinium lines were found. The mixture was, therefore, ytterbium and erbium with some samarium, but no holmium, thulium, or dysprosium, no yttrium, gadolinium, or terbium.

To show further the effectiveness of this method of fractionation, it was tried on nearly all of the material in hand. The material was divided into two parts, in one of which the bases had an atomic weight of 117·37, and in the other of 107·15. Each of these portions was carefully purified by treating the boiling, slightly acid chloride solution with hydrogen sulphide, filtering, boiling to expel hydrogen sulphide, then precipitating with ammonia and washing, dissolving the precipitate in dilute hydrochloric acid, neutralising, and precipitating with oxalic acid solution, stirring the while by blowing air through the solution. The oxalate precipitate was washed with 0·1 per cent hydrochloric acid to remove iron, then with water, dried, ignited, and dissolved in hydrochloric acid. The atomic weights given above were obtained from the material thus purified by precipitating this chloride solution again with oxalic acid, both solutions being boiling hot.

The details of the treatment for the solution ($R^{III} = 117·37$) were as follows:—The chloride solution was divided and placed in three tall cylinders, diluted and precipitated with ammonia. The hydroxides were washed, then dissolved completely in saturated ammonium carbonate solution, and concentrated acetic acid added just to turbidity. Then to each of the three cylinders was added 1000 c.c. of dilute acetic acid (1 part acid diluted to 30 with water) in small quantities at a time, and with constant stirring by a current of air. The flocculent precipitate soon became granular, and could easily be separated from the mother-liquor by decantation. The last of the mother-liquor was removed from this fraction 1 by suction. Dilution with water caused the earths to precipitate from the ammonium carbonate solution; therefore the mother-liquor could not be washed out. The mother-liquors were treated with concentrated hydrochloric acid till the ammonium carbonate was destroyed, and the resulting hydroxides dissolved, then precipitated with ammonia, dissolved in hydrochloric acid, and reprecipitated with ammonia; then these hydroxides were treated again with saturated ammonium carbonate solution. This time the carbonate solution was placed in two cylinders, the excess of ammonium carbonate neutralised by concentrated acetic acid, and 700 c.c. of dilute acetic acid added to each one slowly, and with constant stirring. The precipitate was fraction 2.

The mother-liquors here were removed and decomposed exactly as before, and the ammonium carbonate solution of the hydroxides neutralised with concentrated acetic acid, and treated in one cylinder with about 600 c.c. of dilute acetic acid (fraction 3). The mother-liquor from this fraction still showing a trace of the erbium band in the green after its conversion by the usual decomposition into chloride solution and concentration, it was diluted, precipitated with ammonia, dissolved in saturated am-

monium carbonate solution as before, and precipitated this time after neutralisation by about 30 c.c. of dilute acetic acid. The precipitate (fraction 4) was, of course, slight. The mother-liquor from it was dissolved in hydrochloric acid, nearly neutralised with ammonia, and precipitated with oxalic acid to remove most of the iron. The oxalates were washed, dried, ignited, and dissolved in hydrochloric acid. This solution concentrated to saturation gave three absorption bands, the red and the green of erbium, and the samarium band between the blue and the green, none of them strongly. The atomic weights of the bases for the series were:—

Original, 117·37.

1.	2.	3.	4.	Residual mother-liquor.
115·25	116·33	141·62	159·78	165·48

The other material ($R^{III} = 107·15$) treated in the same manner yielded the following series of atomic weights:—

1.	2.	3.	4.	Residual mother-liquor.
105·33	102·4	110·6	119·45	146·53

It is worthy of note here that the metal atomic weights of the first two of the fractions in each of these series are quite close together, while those of the other fractions show a marked divergence from one another. In the second series the curve of atomic weights even goes through a minimum. There are two reasons for the apparent non-fractionation in these first two fractions. One is that the larger portion of the material used was precipitated in these first two fractions. The other and more important one is that the erbium ($R^{III} = 166$), terbium ($R^{III} = 159$), and yttrium ($R^{III} = 89$) have so distributed themselves in the first and second fractions, more terbium in the first, more erbium in the second, that the atomic weights of the metal mixtures are about the same.

The changes in colour of the ignited oxides from these series were very marked. In the first series the original earth was a deep orange-yellow colour. No. 1 gave a more deeply coloured earth, No. 2 was chamois-coloured, No. 3 pink, No. 4 white with a pinkish cast, and the earth from the mother-liquor almost white. In the second series the earth from the original solution had a deeper orange-yellow colour than that from the other original solution. No. 1 was more deeply coloured yet than this original solution, No. 2 lighter, No. 3 chamois-coloured, No. 4 the same, and that from the mother-liquor white with a pinkish cast.

This colour change evidences a marked change in the terbium content of the various fractions. Terbium concentrates very markedly in the first fractions. It is true that much the larger portion of the earths was thrown out in the first fraction in these two series, but by a short systematic fractionation, erbium material can unquestionably be obtained terbium-free.

This method seems then to offer a method for the comparatively rapid concentration of terbium with yttrium at one end of the series, and of erbium and ytterbium at the other. Holmium, thulium, and dysprosium concentrate in the middle fractions.

The results thus far obtained in this investigation may be briefly summarised as follows:—

The Gibbs method of determining the equivalent weight does not give exact results even when the conditions prevailing in different series of determinations are identical.

There is a slight error in the sulphate method of determining the equivalent weights, due to the formation of some acid sulphate.

Of the many methods of partial precipitation which were investigated the following seem to be the most rapid; primary potassium oxalate, potassium trinitride, partial decomposition by fusion of the nitrates with alkali nitrates, and electrolysis of neutral solutions. Magnesia usta causes fractionation of this material, but the progress of

the separation can not be easily controlled with the spectroscope as was done by Muthmann in his work on didymium.

One of the best methods for the separation of yttria from the other members of this group is that of fractional precipitation of a neutral solution by potassium chromate. Quite pure yttria may be obtained in this manner at the end of a comparatively short series of fractions.

Unusually rapid separation of the earths of this group is effected by ammonium carbonate and acetic acid. Fractional solution of the hydroxides by means of a saturated ammonium carbonate solution causes quite rapid separation, and if this ammonium carbonate solution be fractionally precipitated by addition of acetic acid, the results are most striking. Ytterbium is the last of the earths to be precipitated by this treatment. Erbium and terbium concentrate in the first fraction.

THE ADIO-ACTIVITY OF THORIUM COMPOUNDS.*

I. AN INVESTIGATION OF THE RADIO-ACTIVE EMANATION.

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and

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(Concluded from p. 295).

Effect of Conditions upon Emanating Power.

BEFORE any further work was undertaken, it was necessary to make a close study of the influence of conditions upon the emanating power of thorium compounds.

Effect of Temperature.—The effect of increase of temperature on the emanating power of thorium has already been fully investigated by one of us (*Phys. Zeit.*, 1901, ii., 429). The results, stated briefly, show that an increase in temperature up to a certain limit, in the neighbourhood of a red heat, correspondingly increases the emanating power. At the maximum, this is between three and four times the value at the ordinary temperature, and is maintained at this increased value for several hours without any sign of diminution with time. When the thorium is allowed to cool, the emanating power then returns to the neighbourhood of the normal value. If, however, the limit of temperature given is exceeded, de-emanation sets in, and even while the high temperature is maintained, the emanating power falls rapidly to a fraction of its former value. On cooling, the substance is found to be more or less de-emanated. It is of interest that no increase of emanating power is observed when de-emanation commences.

These experiments were extended to include the effects of cooling. The platinum tube which contained the thorium was surrounded with a felt jacket containing a mixture of solid carbon dioxide and ether. The emanating power immediately fell to 10 per cent of its former value. On removing the cooling agent, it again rose quickly to nearly its normal value.

In another experiment, some thorium was surrounded in a platinum crucible with a mixture of solid carbon dioxide and ether, and kept in a vacuum for several hours. On removing it and allowing its temperature to rise, it possessed much the same value as an ordinary sample, and after standing some time in the air it was again tested and no difference could be detected between the two.

Thus changes in temperature produce very marked simultaneous changes in emanating power, but between the limits of -110° and an incipient red heat no permanent alteration in the value occurs.

Effect of Moisture.—Dorn (*loc. cit.*) had noticed that moisture produced a moderate increase in the power of

thoria of giving an emanation, and of exciting radio-activity on surrounding surfaces. We have confirmed and extended his results by the following experiments:—

Two similar weights of ordinary thorium were exposed in jars sealed with wax, the one containing sulphuric acid and the other water, for a period of four days. The desiccated sample showed 54 per cent, and the sample exposed to water-vapour 134 per cent of the original emanating power. The experiment was repeated and the samples left for a week with much the same result: 70 per cent and 141 per cent respectively. It was of interest to see if a more complete desiccation would further reduce the emanating power. Five grms. of thorium were sealed up in a tube containing phosphoric oxide, the two substances being separated by a plug of glass-wool. Before sealing, the tube was exhausted by a Töpler mercury pump. After twenty-six days the end of the tube was connected with a closely packed phosphoric oxide tube, the tip broken off inside the connection, and a slow stream of dried air thus allowed to enter. The other end was connected to the testing cylinder, and arrangements were made to send a stream of air through into the cylinder. When all was ready, this end of the tube was broken inside the connection, and the emanating power measured. A similar experiment made with an ordinary sample of thorium, using the same arrangement, showed that the desiccated sample possessed 79 per cent of the emanating power of the ordinary sample tested under the same conditions.

A sample of thorium sprayed with water gave 125 per cent of its original emanating power. If completely flooded with water, however, the value is much reduced, as would be expected from the reduction of surface.

Another trial was made, in which thorium was flooded with concentrated sulphuric acid. Hardly any emanation was observed so long as the mixture remained undisturbed, but when vigorously shaken it gave nearly one-half of the original emanation.

These experiments show that the presence of water, although producing a marked increase, is not apparently essential for the production of the phenomena. It must be mentioned, however, that thorium only ceases to lose weight after prolonged ignition with the blowpipe; that is, under conditions which nearly destroy its emanating power. This, with analogous points, will be taken up however, in a separate communication on the more purely chemical side of the question.

The results of some experiments on the effects of other conditions may be shortly tabulated. In each case the sample was exposed to the conditions given for four days. The emanating power is that possessed at the end of this period, compared with that of the first sample, which is regarded as 100 per cent:—

1. Kept in sealed test-tube enclosed completely in lead tube	100 per cent
2. Taken from tightly stoppered stock bottle containing the main quantity	100 "
3. Sealed up in test-tube and exposed to bright all-day sun	100 "
4. Exposed to the air of the laboratory in open watch-glass	105 "
5. Kept in a continuous stream of ordinary air	88 "

The last experiment was made at a different time from the other four, and therefore is not strictly comparable. The most useful result attained is that thorium does not change in emanating power when kept in closed vessels under different conditions, but when exposed to the air the emanating power varies within comparatively narrow limits.

Thorium Hydroxide.—The effect of time on the emanating power of the freshly prepared hydroxide already mentioned is one of the most striking observations in this connection. The following additional experiments have been made on this point. A quantity of hydroxide was prepared, and separate portions subjected to different

* Communicated by the Authors.

drying temperatures and subsequent conditions, as follows :—

	Emanating power.
1. Dried at 110° and exposed some hours to the air	264 per cent
2. Dried as before at 110° and kept in desiccator until tested	226 "
3. Dried at 200° and kept in desiccator..	220 "
4. Dried at 250° and kept in desiccator..	219 "

From this, it appears that the additional loss of water caused by exposure to increasing temperatures is without effect on the emanating power.

A similar experiment to that described for thorium oxide was performed with the hydroxide. Two quantities were exposed in closed bottles to the action of moist air and of air dried with sulphuric acid respectively, and showed, after four days, emanating powers of 394 per cent and 307 per cent. After having been exposed to the air for twenty-four hours, these samples showed 350 per cent and 324 per cent respectively.

The next experiment was designed to include the effect of carbon dioxide, which the hydroxide absorbs from the air to the extent of 2 per cent of its weight. A quantity of hydroxide was tested immediately after preparation, and possessed 140 per cent emanating power. A sample was sealed up in a test-tube, while another similar sample was tested in the following manner. It was exposed to a current of moist carbon dioxide for an hour, and then possessed an emanating power of 156 per cent. It was then left exposed to the air of the laboratory and tested at intervals :—

After two days	Emanating power 263 per cent
After six days.. ..	" 325 "
After ten days	" 300 "
After eleven days	" 341 "
After sixteen days.. ..	" 362 "

On the last day, the sealed-up specimen was opened and examined, and was found to possess an emanating power of 298 per cent. These experiments show that if the air is fundamental in producing the increase of emanating power with time, a very limited quantity of it is effective. For the present, it is perhaps better to consider it as an effect of time simply, hastened no doubt by the presence of water-vapour.

On the Chemical Nature of the Emanation.

The following work has reference to the emanation itself, and not to the material producing it, and was designed to see whether the emanation possesses chemical properties which would identify it with any known kind of matter. It had been noticed at the time of its discovery that it passed unchanged through concentrated sulphuric acid. The same holds true of every reagent that has been investigated.

The effect of temperature was first tried. The air containing the emanation, obtained in the usual way by passage over thoria, was led through the platinum tube heated electrically to the highest attainable temperature, and also through the tube cooled by solid carbon dioxide and ether. The tube was then filled with platinum black, and the emanation passed through in the cold, and with gradually increasing temperatures, until the limit was reached. The effect of the intense heat was to convert the platinum black completely into platinum sponge. In another experiment, the emanation was passed through a layer of red-hot lead chromate in a glass tube. The current of air was replaced by a current of hydrogen and the emanation sent through red-hot magnesium powder and red-hot palladium black, and, by using a current of carbon dioxide, through red-hot zinc dust. In every case, the emanation passed without sensible change in the amount. If anything, a slight increase occurred, owing to the time taken for the gas current to pass through the tubes when hot being slightly less than when cold, the decay *en route*

being consequently less. It will be noticed that the only known gases capable of passing in unchanged amount through all the reagents employed are the recently discovered gases of the argon family.

But another interpretation may be put upon the results. If the emanation were the manifestation of excited radio-activity on the surrounding atmosphere, then since from the nature of the experiments it was necessary to employ in each case, as the atmosphere, a gas not acted on by the reagent employed, the result obtained might be explained. Red-hot magnesium would not retain an emanation consisting of radio-active hydrogen, or red-hot zinc dust an emanation consisting of radio-active carbon dioxide. The correctness of this explanation was tested in the following way :—Carbon dioxide was passed over thoria, then through a T-tube, where a current of air met and mixed with it, both passing on to the testing cylinder. But between this and the T-tube, a large soda lime tube was introduced, and the current of gas thus freed from its admixed carbon dioxide before being tested in the cylinder for emanation. The amount of emanation found was quite unchanged, whether carbon dioxide was sent over thoria in the manner described, or whether an equally rapid current of air was substituted for it, keeping the other arrangements as before. The theory that the emanation may consist of the surrounding medium rendered radio-active is thus excluded, and the interpretation of the experiments must be that the emanation is a chemically inert gas analogous in nature to the members of the argon family.

It is perhaps early to discuss these results from a theoretical point of view, although it appears certain that an explanation of the nature of the emanation must precede, as a necessary step, any hypothesis put forward to account for emanating power. The explanation already advanced and disproved being left out of the question, two other views of the origin and nature of the emanation are still possible. It may be that one of the inert constituents of the atmosphere is rendered radio-active in the presence of thoria, and so constitutes the emanation. The actual amount being probably extremely small, and air being a constant impurity in all gases as ordinarily prepared, it is of course no argument against this view that emanating power is independent of the gaseous medium surrounding the emanating material. An experiment is in progress, however, to ascertain whether emanating power persists in a current of gas as free from air as present methods of preparation allow. The other alternative is to look upon the emanation as consisting of a gas emitted by the thorium compound. It is not necessary that such should contain thorium, it might conceivably be an inert gas continuously emitted in the radio-active state.

In the present state of knowledge, it would be premature to attempt to choose between these two alternatives. But in any decision of this point, the work already given on the regeneration of the emanating power of thoria de-emanated by ignition, the continuous loss of emanating power by successive ignition at increasing temperatures, and the increase in the chemical activity of thorium hydroxide with time, must be taken into consideration.

Concentration of the Radio-active Material.

Since the preceding account was written, developments have been made in the subject which completely alter the aspect of the whole question of emanating power and radio-activity. The first has reference to thorium nitrate, which in the solid state hardly possesses any emanating power. In a careful determination, using 20 grms. of the finely-powdered commercial salt, this worked out to be only 1·8 per cent of the emanating power of thoria. Dissolved in water, however, and tested for emanation by bubbling a current of air through it, it gives about three times as much emanation as thorium oxide; that is, solution in water increases the emanating power of thorium nitrate nearly two hundred times. The emanating power, as in the case of solids, is proportional to the weight of

substance present, and within the limits tried is not much affected by dilution, for a solution of 10 grms. made up to 25 c.c. in volume possessed a similar value when diluted four times.

Solutions of thorium chloride also give a large amount of emanation.

In these experiments, the cylinder c (Fig. 1) is replaced by a Drechsel bottle. A drying tube of calcium chloride is inserted between it and the testing cylinder to prevent the moisture destroying the insulation of the latter. In this connection, the method of testing the insulation by varying the voltage is invaluable. The air current under these circumstances cannot of course be kept so constant as when working with solid substances, and the results are not strictly comparable in consequence, but the arrangement works well enough for a first approximation.

Simultaneously with this observation of the latent emanating power of thorium nitrate, it was noticed that preparations of thorium carbonate varied enormously in emanating power according to their method of preparation. A sample prepared from the nitrate by complete precipitation with sodium carbonate showed an emanating power of 370 per cent of that of the ordinary oxide, and this value remained fairly constant with time. In another experiment, the precipitated carbonate was partially re-dissolved in nitric acid, and the re-dissolved fraction completely re-precipitated with ammonia as hydroxide. The result was remarkable; the carbonate had an emanating power of only 6 per cent, the hydroxide one of 1225 per cent of that of the ordinary oxide. On repeating the experiments, both fractions proved almost equally inactive, the carbonate showing 14 per cent and the hydroxide 19 per cent of the emanating power of thoria. An even greater difference between these two similar experiments was observed in the effects of time on the different preparations. In the first, the carbonate did not alter in value in seven days, whilst the hydroxide steadily decreased:—

	Hydroxide. Per cent.	Carbonate. Per cent.
Original	1225	6.2
After one day	1094	8.4
After four days .. .	696	4.8
After seven days .. .	614	4.7
After fourteen days ..	473	—

In the second experiment, the emanating power of both the carbonate and hydroxide had increased many fold when tested eleven days later, and the former now possessed 109 per cent, the latter 273 per cent (originally 14 per cent and 19 per cent respectively).

The straight-line radio-activity of the carbonate from the first experiment which possessed such a low emanating power is of interest. It proved to be similar to that of a specimen of hydroxide of normal emanating power, which it resembled in density and state of division. After having been kept seven days without showing any sign of recovering its emanating power, it was re-dissolved in nitric acid, and re-precipitated with ammonia as hydroxide. The latter now possessed, when first made, an emanating power of 65 per cent, and after twenty-four hours 145 per cent, from which value it did not much alter.

These results throw a new light on the question of emanating power. In the first experiment, which we have so far not succeeded in repeating, by an accident in the conditions apparently, two fractions were separated from thorium which varied in their emanating power in the ratio of 200 to 1. The active fraction diminished to nearly a third of its original value in fourteen days spontaneously, whilst the activity of the inactive fraction was, to a large extent, regenerated by solution and re-precipitation, in an exactly analogous manner to the behaviour of thoria de-emanated by ignition. Attempts to repeat this result have so far led to the production of two more or less completely de-emanated fractions, which, however, spontaneously increase in activity with time, as in the

second experiment, and this seems to be generally the case, whether incomplete precipitation is effected as in the experiment given by re-solution of the carbonate in acid, or by using a deficiency of sodium carbonate in the first instance.

The production of preparations of such low emanating power led naturally to an examination being made of the filtrates and washings for radio-activity. It was found that these possess when concentrated both emanating power and radio-activity in considerable amounts, although from the nature of their production they should be chemically free from thorium. The behaviour is quite general, a dilute solution of thorium nitrate, after the thorium has been precipitated as hydroxide with ammonia, shows, when concentrated, an emanating power of from one-third to two-thirds that of the original nitrate in solution. It does not matter whether the thorium is precipitated with ammonia directly, or after preliminary partial precipitation as carbonate—either by adding insufficient sodium carbonate in the first place, or by precipitating completely and dissolving part of the precipitate in nitric acid—the thorium-free filtrate invariably possessed emanating power, and when evaporated to dryness exhibited straight line radio-activity also in amounts very much greater than possessed by the same weight of thoria.

The result of a careful chemical investigation of the active filtrates produced under the various conditions described, was to show that these contained no thorium, or at most only a minute trace, but another substance in very appreciable quantities which can be precipitated with sodium phosphate, and which so prepared is a white substance possessing both emanating power and radio-activity, often many hundredfold greater than thoria. It has not yet been obtained in sufficiently large quantities for an exhaustive chemical investigation, and it is impossible at present to say what it may prove to be.

We may at once state, however, that we do not incline to the view that it is ThX either in the sense of the radio-active or emanating constituent of thorium. The evidence of a long series of experiments in two directions, of which the final steps can only find place here, is quite definite on this point, and in our opinion admits of only one conclusion. There seems little doubt of the actual existence of a constituent ThX to which the properties of radio-activity and emanating power of thorium must be ascribed, but in all probability it is present in altogether minute amount, and must therefore be possessed of these qualities to a correspondingly intense degree.

But before the reasons for this view are put forward, it is necessary to discuss more nearly the meaning of the experiments already given on the emanating power. It has been shown that this is a most uncertain quantity, similar experiments often giving preparations of very varying value, as is clearly shown in the results given, as well as in many others in the same direction. The most pregnant fact is, that although, as has been shown, precipitation with ammonia invariably leaves behind considerable emanating material in the filtrate which is lost, this seems to exert little influence on the emanating power of the precipitates. These prepared under different conditions, often by a different number of precipitations, in which therefore varying amounts of the emanating material are lost, show a surprising uniformity in this property, especially after they have attained their maximum power by keeping. It is only necessary to quote the experiment on the almost completely de-emanated carbonate, which gained in emanating power thirty times by conversion into the hydroxide, although during the process much emanating material must have been lost, to show that the value of the emanating power alone furnishes no criterion of the amount of emanating material present.

It may safely be said that three things must be carefully distinguished between in considering the nature of the property possessed by thoria of giving out a radio-active

emanation. First, the nature of the emanation itself; secondly, the nature of the emanating power; and thirdly, the nature of the emanating material. The first, the emanation itself, we have shown to possess the negative properties of a chemically inert gas, whose radio-activity is unaffected by any conditions apparently except lapse of time. With regard to the second—the emanating power, or rate at which the emanation is produced per unit weight of substance—it is certain that this does not depend only or even mainly on the quantity of emanating material present. The regeneration of the emanating power of thorium de-emanated by ignition, the enormous variation with time in the emanating power of the hydroxide and carbonate under certain conditions, and the comparatively constant maximum which these substances ultimately attain, although prepared under conditions where different amounts of the emanating material are lost, make this point perfectly clear. These considerations, taken in conjunction with the effect of temperature, moisture, &c., on emanating power, and the nature of the emanation itself, make the property appear rather as the result of a dynamical change, possibly in the nature of a chemical reaction where the active mass of emanating material is a constant—than as the property of a peculiar kind of matter in the static state, additive with regard to mass.

It is, however, neither the emanation itself nor the emanating power with which we are concerned in these experiments, but the third conception—the emanating material, *i.e.*, the substance, whether thorium or not, which is responsible for the activity. It has been shown that it is difficult to follow by means of the value of the emanating power, the progress of the removal of the active material. When this was realised, attention was directed to the straight line radio-activity, which is generally unaffected by these changes of conditions and previous history which produce such profound alteration in the former property. The two phenomena are undoubtedly connected. The intensely radio-active preparations obtained from thorium in different ways always show correspondingly great emanating power, when the conditions are favourable for the manifestation of the latter. Solution appears to be the most generally favourable condition. The experiments we had been engaged in were therefore repeated in a form which would allow a close study of the total radio-activity, in the hope that this value would prove a more suitable indication of the amount of active material present than the emanating power alone.

Seventy grms. of thorium nitrate were dissolved in 4 litres of boiling water, and precipitated with ammonia added cautiously in very dilute solution in excess. The filtrates and washings were evaporated to about 60 c.c., and then possessed as much emanating power as 146 grms. of thorium. On evaporating the solution to dryness and removing the ammonium salts by ignition, the residue weighed 0.0583 gm. The emanating power of this residue in solution was thus about 2500 times that of ordinary thorium. In the solid state, however, the value fell to one-fiftieth. But its total radiation was equivalent to at least 23.6 grms. of thorium, *i.e.*, was about 400 times as great. It was dissolved in hydrochloric acid, and ammonia added in excess, when a precipitate weighing 0.0015 gm. was thrown down. This contained all the thorium present besides iron in appreciable quantity which had been introduced during the evaporation. It equalled in radio-activity 2.73 grms. of thorium, the ratio in this case being thus no less than 1800 times. Sodium phosphate precipitated 0.0225 gm. of white substance the activity of which was equivalent to 4.4 grms. of thorium, *i.e.*, 200 times. The sodium salts freed from ammonium still possessed a radio-activity equivalent to 3.6 grms. of thorium oxide. In other experiments, however, these had been obtained quite free from activity, and this result is due to the solubility of the phosphate in water, so that some was dissolved during the washing (which the subsequent determination of the weight rendered necessary), and appeared in the filtrate.

The radio-active residue obtained in the first place from the filtrate by evaporation and ignition, before it was re-dissolved, had, however, been tested to determine the penetrative power of the radiations emitted. If the rays from various radio-active substances are made to pass through successive layers of aluminium foil, each additional layer of foil cuts down the radiation to a fraction of its former value, and a curve can be plotted with the thickness of metal penetrated as abscissæ, and the intensity of the rays after penetration as ordinates, expressing at a glance the penetrative power of the rays being examined (compare Rutherford, *Phil. Mag.*, 1899, [5], xlvii., p. 122). The curves so obtained are quite different for different radio-active substances. The radiations from uranium, radium, thorium each give distinct and characteristic curves, whilst that of the last named again is quite different from that given by the excited radio-activity produced by the thorium emanation. The examination in this way of the penetrative power of the rays from the radio-active residue showed that the radiations emitted were in every respect identical with the ordinary thorium radiation. In another experiment, the nature of the emanation from a similar intensely active thorium-free residue was submitted to examination. The rate of decay was quite indistinguishable from that of the ordinary thorium emanation. That is, substances chemically free from thorium have been prepared possessing thorium radio-activity in an intense degree.

The main quantity of thorium hydroxide in the last experiment was re-dissolved in nitric acid, and the previous round of operations repeated twice, the filtrates from each operation being mixed and then examined exactly as in the former case. The emanating power of the concentrated solution was only equal to that of 8 grms. of thorium in this instance, and the radio-activity of the residue to that of 3 grms. From this only a small quantity of the phosphate precipitate was obtained (0.001 gm.), the radio-activity of which was equal to that of 0.3 gm. of thorium (ratio 200 : 1).

The emanating power of the main quantity of the hydroxide when first so prepared was 73 per cent that of thorium, *i.e.*, about one-half of its usual value. The hydroxide was converted into oxide by ignition, and its radio-activity compared with that of the oxide from the original nitrate prepared in the same way. It was found to be only about one-third as active, the exact ratio being 0.36 : 1.

Only one conclusion seems possible from this series of experiments. There is no longer any room for doubt that a part of the radio-active constituent ThX has been separated from thorium, and obtained in a very concentrated form, in one instance 1800 times more powerful in its actions. This result, taken into account with the reduction of the radio-activity and emanating power of the main quantity of thorium compound, and the identity of the radiations of the active thorium-free preparations with those of the ordinary thorium radiation, warrant the conclusion that ThX is a distinct substance, differing from thorium in its chemical properties, and so capable of separation therefrom. The manner in which it makes its appearance, associated with each precipitate formed in its concentrated solution, resembles the behaviour of Crookes's UrX, which he found was dragged down by precipitates when no question of insolubility is involved, and suggests the view that it is really present in minute quantity. Even in the case of the most active preparations, these probably are composed of some ThX associated with accidental admixtures probably large in proportion.

These results receive confirmation from observations made in a different method of separating ThX. The experiment was tried of washing thorium with water repeatedly, and seeing if the radio-activity was thereby affected. In this way it was found that the filtered washings on concentration deposited small amounts of material, with an activity often of the order of a thousand times greater than that of the original sample. In one experiment 290 grms.

of thoria were shaken for a long time with nine quantities, each of 2 litres, of distilled water. The first washing containing most of the sulphate already referred to was rejected, the rest concentrated to different stages, and filtered at each stage. One of the residues so obtained weighed 6.4 m.grms., and was equivalent in radio-activity to 11.3 grms. of the original thoria, and was therefore no less than 1800 times more radio-active. It was examined chemically, and gave, after conversion into sulphate, the characteristic reaction of thorium sulphate, being precipitated from its solution in cold water by warming. *No other substance than thorium could be detected by chemical analysis*, although of course the quantity was too small for a minute examination. But the absence of the substance precipitable as phosphate, noticed in the other experiments, confirms the opinion that this is an accidental admixture without influence on the qualities of radio-activity and emanating power. The penetrative power of the radiation from this substance again established its identity with the ordinary thorium radiation. In another experiment a small quantity of thoria was shaken many times with large quantities of water. In this case the radio-activity of the residue was examined and found to be about 20 per cent less radio-active than the original sample.

There remains only one step to prove beyond doubt that the radio-activity and emanating power of thorium are not specific properties of the thorium molecule—the preparation of thoria free from these properties—and on this problem we are now engaged. To sum up briefly what has already been accomplished, two different methods have effected a concentration of the activity many hundredfold in one fraction, and a corresponding diminution of activity in the remainder, but in each case the character of the radiation is not thereby affected. In one method, the active fraction appears to consist only of thorium, so far as examination has been possible, whilst in the other case radio-activity and emanating power appear to be manifested indiscriminately in all the products, without reference to their chemical nature. The simplest explanation of this behaviour on the present view, is that so far the active constituent of thorium has only been obtained in relatively minute quantity, and therefore does not answer to any definite analytical reactions.

Macdonald Physics Building,
Macdonald Chemistry and Mining Building,
McGill University, Montreal.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several

samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us chemically during the month, all were found to be clear, bright, and well filtered.

Although more rain has been recorded at Oxford during the past month it was below the average, and there is still a deficiency. The amount of rain that fell was 1.53 inches, the thirty-five years' average for May is 1.75 inches, making a deficit of 0.22 inch, which, added to the previous one, makes a total deficit for the year of 3.16 inches, or 36.2 per cent on the thirty-five years' average.

The various chemical analyses show that the organic matter has steadily decreased in amount since the beginning of March.

Our bacteriological examinations of 544 samples have given the results recorded in the following table; we have also examined 47 other samples, from special stand pipes, wells, &c., making a total of 591 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	193
New River, filtered (mean of 135 samples) ..	12
Thames, unfiltered (mean of 26 samples) ..	2896
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 295 samples) ..	31
Ditto ditto highest	398
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	371
River Lea, from the East London Company's clear-water wells (mean of 36 samples) ..	37

A sample has been taken daily from the large filter-wells of each of the Metropolitan Companies, as has been our custom for some years. The total number of samples from all sources examined in this way during the month amounted to 446, of which 27 samples, or 6 per cent, were sterile. Twelve samples contained more than 150 microbes, while thirty samples, or 6 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the thirty excess samples was 173, against a corresponding mean of 181 in thirty-one excess samples during April.

These figures show an improvement in the bacteriological quality of the London waters since April, in spite of the fact that during the last month there has been more rain in the valley of the Thames than has fallen for some time past, with the concomitant result of more surface water flowing into the river, bringing with it additional impurity.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

Preparation of Anhydrous Chlorides of Samarium, Yttrium, and Ytterbium.—Camille Matignon.—The preparation of anhydrous chlorides of the rare earths in a pure state is a very delicate operation. M. Duboin for yttrium, and MM. Muthmann and Stütz for cerium, lanthanum, and the didymiums, showed that the dehydration of the hydrated salts in presence of ammonium chloride never gives a product free from oxychloride. The author now uses the method he employed to obtain anhydrous chlorides of neodymium and praseodymium (*Comptes Rendus*, cxxxiii., 289) to prepare chlorides of the other rare earths, and succeeds in preparing the anhydrous salts of samarium, ytterbium, and yttrium, the first two of these never having previously been obtained. He also finds an ytterbium chloride, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, isomorphous with that of yttrium, and proves the existence of the three monohydrated chlorides, $\text{SmCl}_3 \cdot \text{H}_2\text{O}$, $\text{YCl}_3 \cdot \text{H}_2\text{O}$, and $\text{YbCl}_3 \cdot \text{H}_2\text{O}$.—*Comptes Rendus*, cxxxiv., No. 22.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, May 28th, 1902.

Prof. MELDOLA, F.R.S., Vice-President, in the Chair.

(Concluded from p. 298).

85. "On Phosphorus Sesquisulphide and its Behaviour with Mitscherlich's Test." By E. G. CLAYTON, F.I.C.

Many compounds of phosphorus and sulphur have been described, but of these the only one which has received any application on the large scale is the sesquisulphide, P_4S_3 , discovered by Lemoine in 1864. When pure, it is a lemon-yellow crystalline solid, with a strong odour of hydrogen sulphide, soluble at 15° in 1.6 parts of carbon bisulphide, and igniting in the air at about 100°. Commercially, several qualities of this substance are manufactured. Amongst those which have come under observation have been a coarsely granular lemon-yellow powder, a fine-grained yellow powder of somewhat duller tint, and a grey product, sometimes very impure. The following are typical analyses:—

	A. Yellow (fine- grained).	B. Yellow (fine- grained).	C. Yellow (coarse grained).	D. Grey (finely granular).
Water and volatile matter (loss at 100° in an atmo- sphere of carbon dioxide)	0.19	0.18	8.74	7.31
Phosphorus sesquisulphide, P_4S_3	97.86	97.62	84.95	83.34
Red phosphorus.. .. .	—	—	—	1.81
Phosphoric acid, H_3PO_4 ..	1.30	1.63	2.14	1.23
Sulphur, uncombined (sol- uble in carbon bisulphide)	—	—	4.17	—
Sulphur, uncombined (in- soluble in carbon dioxide)	0.46	0.40	—	0.17
Calcium phosphate	—	—	—	3.35
Calcium sulphate	—	—	—	0.27
Iron oxide, &c.	—	—	—	1.72
Siliceous matter	0.19	0.17	—	0.80
	100.00	100.00	100.00	100.00

Temperature at which the specimen became lumin- ous in the dark	92°	93°	—	58°
Temperature of ignition ..	94°	96°	86°	72°
Reaction with Mitscher- lich's test	Nega- tive.	Nega- tive.	Dis- tinct.	Dis- tinct.

Mörner has recently stated (*Svensk Farmaceutisk-Tidskrift*, 1901, xii., 177) that phosphorus sesquisulphide gives "more or less positive results" with Mitscherlich's test for phosphorus. The author has examined various specimens of commercial phosphorus sesquisulphide, and applied Mitscherlich's test to each in the following way:—Twenty grms. of the compounds were distilled with 100 c.c. of 10 per cent sulphuric acid, in an egg-shaped flask connected with a spiral condenser, the operation being conducted in a dark room. The very small amount of light emitted by the lamp was screened from the condenser and receiver, which were in complete darkness. In each case, 40 c.c. of liquid were distilled over. The results with comparatively pure specimens, such as A and B, were absolutely negative, not the faintest luminosity being perceptible in any part of the apparatus. It is evident that pure, or even approximately pure, phosphorus sesquisulphide gives no reaction with Mitscherlich's test, and that Mörner's results were obtained with samples containing small quantities of phosphorus, or of phosphorous oxide. Very crude specimens of phosphorus sesquisulphide no doubt occasionally give Mitscherlich's reaction; thus, with the im-

pure specimen, D (tested after being kept for many months in the laboratory), a distinct luminous cloud played about the exit of the condenser, and in the air of the receiver above the surface of the distillate, which had a faint odour of phosphorous oxide. The sample C, which had been kept for nearly three years, and had undergone considerable oxidation, being quite moist, also gave a decided reaction. The distillate from this also smelt distinctly of phosphorous oxide. The specimens A and B, which gave negative results, had been recently made. Even in these samples some oxidation had occurred, but apparently no phosphorous oxide was present. The author is now conducting some experiments with the object of discovering whether exposure and keeping can so induce partial oxidation in, or alter the composition of, pure, or nearly pure, phosphorus sesquisulphide as to impart to it after a time the property of giving Mitscherlich's reaction. Apart from its scientific interest, the point was of considerable practical importance. Meanwhile, the absence both of free phosphorus and of phosphorous oxide from phosphorus sesquisulphide of fair quality and purity and comparatively recent manufacture was clearly indicated by the negative reaction with Mitscherlich's test, and the following circumstances were corroborative as far as they went. Phosphorus sesquisulphide may be subjected to friction in air at a temperature very considerably exceeding the ignition-point of phosphorus without becoming luminous, and with a total absence of "phosphorus fume"; it neither ignites nor begins to glow in the dark until a temperature of 92—96° is reached, and the finely-divided residue of a solution in carbon bisulphide, evaporated on filter-paper at the ordinary temperature, neither glows in the dark, fumes, nor ignites spontaneously.

86. "Atomic and Molecular Heats of Fusion." By P. W. ROBERTSON.

No satisfactory relationship has hitherto been found connecting the latent heat of fusion of substances with their atomic or molecular weights. In the case of the elements, the following is shown to yield satisfactory results:—"For the elements with atomic weights above 40 which do not expand on freezing, the atomic heat of fusion divided by the melting-point on the absolute scale into the cube-root of the atomic volume is a constant." That is,—

$$Aw/T\sqrt[3]{V} = \text{constant.}$$

The numbers have a mean variation of ± 10 per cent. The only exception is lead, for which the value of the expression is 25 per cent below the mean.

In the case of the binary inorganic compounds also, the expression—

$$Mw/T\sqrt[3]{V},$$

where V is the specific volume of the solid, yields concordant results. The values of the expression for organic compounds increase with the number of atoms in the molecule, but when compounds of similar constitution are considered, fairly constant results are obtained.

To test these relations, the latent heats of the following substances were determined:—

Thallium	7.2	Phenanthrene ..	25
Lead	6.45	Phenylacetic acid	32
Tin	14.05	Tribromophenol .	13.4
Dinitrobenzene ..	29.0	Tribromoaniline .	14.4
		Thiosinamine	33.4

87. "The Preparation of Mixed Ketones by Heating the Mixed Calcium Salts of Organic Acids." By E. B. LUDLAM.

A device for preparing a simple ketone from the calcium salt of the corresponding organic acid was described by Young (*Trans.*, 1891, lix., 623), which consisted in decomposing the salt at the temperature of boiling sulphur and removing the products by a stream of carbon dioxide.

The author has extended the method to mixtures of calcium salts with very satisfactory results.

The conclusions arrived at are—(1) That the decomposition is not of one molecule, but of two; (2) there is a greater tendency towards the production of the mixed than of the simple ketone; (3) that, for economy, it is advisable to distil the more expensive salt with excess of the cheaper one. By so doing the yield of mixed ketone from a given weight of the expensive salt is increased.

88. "Isomeric Additive Products of Methyl, Ethyl, and Propyl Benzyl Ketone with Benzylidene Aniline." Part IV. By F. E. FRANCIS and E. B. LUDLAM.

The benzylideneaniline additive products of methyl, ethyl, and propyl benzyl ketones were prepared in the expectation that they would furnish evidence as to the constitution of the tautomeric forms which such compounds are capable of assuming. Methyl benzyl ketone contains the group $\text{CH}_3\text{CO}\cdot\text{CH}_2-$, which in ethyl acetacetate gives rise to the tautomeric form $\text{CH}_3\text{C}(\text{OH})\cdot\text{CH}-$, and it was hoped that the work would have contributed to the solution of the problem of the constitution of the tautomeric forms of that compound.

Methyl benzyl ketone gave with benzylideneaniline an additive product melting constantly at 173° (α). This, under the influence of piperidine, gave the β -modification melting at 182° , and another modification melting at 184° when subjected to the action of a trace of sodium ethoxide. The hydrochloride of the α -modification was unstable; it gave no fixed melting-point, but slowly decomposed between 140° and 190° . Propyl benzyl ketone gave a similar α -product, crystallising in silky needles melting at 136° , rising to 142° under the influence of piperidine, and to 143° with sodium ethoxide. Ethyl benzyl ketone gave an α -product melting at 161° , intermediate between 136° and 173° . Neither the original ketones nor any of the additive products gave any colouration with ferric chloride, and the melting-points of the β - and γ -varieties fell when they were re-crystallised from pure benzene. They were thus too unstable to serve the purpose for which they were prepared.

89. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part III. Influence of Benzene, Toluene, o-Xylene, m-Xylene, p-Xylene, and Mesitylene on the Rotation of Ethyl Tartrate." By T. S. PATTERSON.

It was found that in dilute solution the influence of benzene is to lower slightly the specific rotation of the dissolved ethyl tartrate. Toluene has a greater influence of the same kind, and this influence becomes greater and greater in the other solvents in the order in which they are placed above.

It was found also that in benzene, toluene, o-xylene, and m-xylene there exists, not only a concentration of minimum rotation, but also one of maximum rotation, which lies at a greater dilution. The concentration-rotation curves for p-xylene and mesitylene show only a point of inflection.

The relationship between molecular-solution-volume and rotation has been investigated, and it was found that in general, although not without exception, the behaviour was the same as in the monohydric alcohols; when the dissolved ethyl tartrate has a molecular-solution-volume greater than the molecular volume of the pure ester the rotation is correspondingly low.

The relationships between rotation, latent heat of vaporisation of the solvent, and surface-tension of the solvent were also discussed.

90. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part IV. Influence of Naphthalene on the Rotation of Ethyl Tartrate." By T. S. PATTERSON.

Naphthalene was found to differ greatly in its behaviour from the benzene hydrocarbons. It has the effect of greatly increasing the rotation of the dissolved ethyl tartrate, and its influence is similar to that of water in this respect as well as in the effect of temperature change.

CORRESPONDENCE.

VALENCY AND RADIO-ACTIVITY.

To the Editor of the Chemical News.

SIR,—I trust you will permit me to publish the skeleton of a theory connecting valency with the property of radio-activity, which I have been elaborating since the end of 1900. The first communication I made to your columns on this matter was a letter which appeared in the CHEMICAL NEWS of March 15th, 1901 (vol. lxxxiii., p. 130). In that letter the term "ion" should be replaced by "electron."

So many authors have lately been approximating to these views that I feel it would be dangerous to delay publishing this preliminary note until I have completed the experiments to confirm or disprove it that I am carrying out in the physical laboratory here—experiments which, from the nature of the case, must occupy a considerable time.

The degree of valency that an elementary atom manifests is conditioned by the number of electrons it contains, according to the universally accepted theory of Helmholtz. For instance, an atom of iodine is tri-valent when there are condensed on its surface three negative electrons, while it is mono-valent when it holds but one. So that a change from a tri-valent to a mono-valent condition must be attended with the loss of two negative electrons.

But a consideration here forces itself on our attention. Electrons are of two kinds—positive and negative. The same atom contains both kinds, and in general different numbers of each. This is shown by the fact that one and the same atom acts with a quite different degree of valence towards positive and negative radicals, as Mendeleeff long ago pointed out. Further, quite a definite law is followed in this matter. If n represent the number of positive electrons and n' the number of negative, Mendeleeff found in any one case that $n+n'=8$.

These positive and negative electrons do not, in the same atom, combine with each other and neutralise one another's effect, but each set apparently retains its position on the atom as if the other set were absent, so far as can be judged from the phenomena of chemical combination.

Again, the same atom has in general a different attractive power for the two different kinds of electrons, some atoms attracting positive electrons with a force greater than that which they attract negative, and *vice versa*. To this cause Helmholtz referred the difference of potentials developed when two different metals are placed in contact.

Metals hold negative electrons with a far greater degree of feebleness than non-metals.

If, therefore, radio-activity is produced by the giving off of electrons this emission could be produced from them in two ways:—

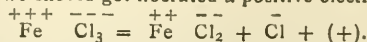
1. By heating up the element. This by increasing the kinetic energy of the electrons would cause them ultimately to be cast forth by the atom. I have considered this point in a previous communication.
2. By a change of valency of the element in combination.

It is the last point I wish to consider here.

In general, when a metallic atom enters into combination with another more negative atom, it is the positive electrons on the first atom that are in the main responsible for the union; e.g., the combination, FeCl_3 , may be repre-

sented thus, $\text{Fe}^{+++} \text{Cl}_3^{-}$. It might be concluded, therefore, that if by some means we reduced the valency of the iron

atom from Fe to Fe, keeping the valency of the Cl constant, we should get liberated a positive electron thus:



But the case is far more complicated than this. (a) In the first place Professor J. J. Thomson has shown that

the mass of the positive electron is great compared to that of a negative electron, and it may be doubted whether free positive electrons are ever thrown off from the atom, or could be, since there is reason to believe that what is known as "positive" electricity is a fundamental property of the matter forming the atom, in the same way that gravity is.

So that when Fe is reduced to Fe⁺⁺, as in the preceding compounds, it may be justly doubted whether there is a loss of electrons. It seems much more probable that there is an addition of negative electrons to the iron atom over and above that which it normally holds in the ferric condition, and which has the effect of masking the action of a positive valency bond.

So that the operation of reducing Fe to Fe⁺⁺ is not to be represented thus: $\text{Fe} = \text{Fe}^{++} + (+)$; but rather thus: $\text{Fe} + (-) = \text{Fe}^{++}$.

A reduced atom is therefore often to be regarded as suffering, not from a deficiency of electrons, but rather from an excess of electrons of an opposite polarity. Since at normal temperatures each atom can retain eight electrons, irrespective of sign, any number above this would be held with great feebleness.

So that on heating up the reduced Fe atom we should get off the added negative electrons. In support of this view I urge the following facts:—

1. When cathode rays fall on a chemical compound they reduce the central element to a lower degree of valence.
2. When compounds thus reduced are heated up to a temperature of 100° or more they throw off again the negative electrons thus supplied (*vide* McLennan, *Phil. Mag.*, 1902, [6], iii., 195—203).
3. Russell has shown that unsaturated carbon compounds often throw off an emanation that affects a photographic plate in the same way that radio-active bodies do (*vide* CHEMICAL NEWS, 1897, lxxv., 302; 1898, lxxvii., 163; 1899, lxxix., 121, 133; lxxx., 288).

I hope to begin experiments on this subject shortly.

(b) In the second place, there is grave reason to believe that when one atom combines with another, both the positive and negative electrons contained on each atom come into play. For instance, when an atom, A, combines with another decidedly more negative atom, B, it acts with one degree of valence. And when it combines with a decidedly more positive atom, C, it acts with a totally different degree of valency. In the first case the positive electrons of A are mainly instrumental in deciding the union; in the second case its negative electrons.

If now this atom, A, enter into combination with another atom, D, which is intermediate in electrical polarity between the extreme positive and negative atoms B and C, A will act with a valence intermediate between the valencies which it exhibits towards B and C.

It seems, therefore, in this case, that both the positive and negative electrons contained in A come into action with the negative and positive electrons contained in D. This is probably quite a general phenomena.

A chemical combination therefore is no simple affair. It is a complicated dual reaction between the positive and negative electrons contained on each atom—the complication being increased by the fact that the electrons of opposite polarity are retained on one and the same atom with very different degrees of stability, so that we may get a surging of negative electrons to one atom, and, consequently, the appearance of positive electrons on the other atom, in a manner that makes it difficult to say what would precisely happen were the valency of the elements forming the compounds reduced.

One fact, however, stands out clearly.

Metals hold electrons, negative electrons at least, with a very much greater degree of instability than non-metals, as is seen, not only in their power to conduct electricity,

but also in the unstableness of their compounds, as is seen in the readiness with which they dissociate in solution; the stability of the union being in the main decided by the stability with which the negative electrons are retained by the metallic atom.

Therefore, if radio-activity is conditioned by the emission of negative particles, a gentle warming of a compound formed by the union of one metal with another should lead to the evolution of such particles from the first metallic atom, as the compound progressively dissociates with the rising temperature, and therefore as the first metallic atom becomes reduced to a lower degree of valence.

1. The fact that Hg when contaminated by a trace of Na or Zn becomes capable of acting readily on a photographic plate in the dark confirms this view. I am carrying out experiments on this subject in the physical laboratory here.
2. When H₂O₂ decomposes into H₂O and O, the hydrogen atom is probably changing its valence from 2 to 1, and therefore may be expected to evolve electrons. I am at present engaged in looking for this effect. The fact that (a) it gives off an emanation which acts on a photographic plate in the same way that radio-active bodies do (*vide* Russell; I have repeated and confirmed his observations); (b) and that it rapidly loses a charge of negative electricity from its surface when undergoing decomposition (*vide* D'Arcy, *Phil. Mag.*, 1902, [6], iii., 42—45) makes this view extremely probable.

The preceding is a mere outline of the general theory. I may say I would not have ventured on this note until I had completely proved or disproved it by experiment were it not that several papers have recently appeared in which there is a distinct approximation to such ideas—I am, &c.,

GEOFFREY MARTIN.

University of Berlin, June 10, 1902.

NOTICES OF BOOKS.

The Hydro-metallurgy of Copper; Being an Account of Processes Adopted in the Hydro-metallurgical Treatment of Cupriferous Ores, Including the Manufacture of Copper Vitriol; with Chapters on the Sources of Supply of Copper and the Roasting of Copper Ores. By M. EISSLER, M.E., Member of the Institute of Mining and Metallurgy. London: Crosby Lockwood and Son. 1902. Pp. 228.

THE hydro-metallurgical treatment of copper ores was originated at the Rio Tinto mines several centuries ago. Several processes have since been evolved, principally through the investigations of manufacturers of sulphuric acid, who made it a special study to extract the low residual percentage of copper from the burnt pyrites and cinders. The application of the various lixiviation processes resulting from the successful solution of the problem of leaching low-grade copper ores are likely to have more attention given to them now, owing to the growing necessity of working the low-grade copper deposits in various parts of the world.

The author makes no claim to originality in the present work, but he has collated and described the various processes now known to be in operation in an admirable manner, though detailed information has often been denied to him for obvious commercial reasons.

The book is divided into three parts and seventeen chapters. Part I. is on the production of copper and its sources of supply, and includes not only wet but dry smelting processes. Part II., which forms the main feature of the work, is on methods of hydro-metallurgical treatment of copper. Under favourable circumstances ores which contain only $\frac{1}{2}$ or 1 per cent of copper are treated by these methods, especially when their treat-

ment is in connection with some other industries, such as the manufacture of sulphuric acid. Not every low-grade copper ore is found to be adapted to hydro-metallurgical treatment, owing to impurities which interfere with the chemical reactions, those most suitable being poor oxides and sulphides in a quartz gangue. Rich by-products, matte, black copper, &c., are treated by the wet process, as well as ore heaps which have undergone decomposition by atmospheric agencies, and mine waters from copper-mines.

The wet processes for the treatment of copper ores are employed for:—(1) Ores which contain the copper as oxides or carbonates; (2) those which contain the copper as a sulphate; and (3) those which contain the copper as a sulphide. The oxides of the first class are usually found associated with carbonates. Soluble sulphates also are rarely found in large quantities, but are formed as mentioned above by atmospheric influences. The third class, the sulphides, are roasted and rapidly converted into a soluble condition.

The author then goes on to explain the various methods adopted for special ores, and the means of recovering the copper from solution. Part III. is on the roasting of copper ores, and includes a large number of diagrams of furnaces and appliances in use for this purpose.

The book is well written, and will undoubtedly be of interest and use to those engaged in the copper industry, especially to students, who will find a large amount of information given in a clear and straightforward style.

There is an index, though not a very extensive one.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 22, June 2, 1902.

Electro-capillary Properties of Organic Bases and their Salts.—M. Gouy.—In a previous research the author showed that salts of the same acid give in equivalent solutions electro-capillary curves differing very slightly from one another whatever the base of the salts used. He now extends this investigation to salts of organic bases and also sulphates, phosphates, and bromides. The effect produced can be analysed more in detail by operating on mixtures. For example, a normal solution, L_1 , of H_2SO_4 is taken and its electro-capillary curve traced. The greatest curve is obtained with Hg_2SO_4 in a normal solution of Na_2SO_4 , which remains unchanged. To L_1 a small quantity of a base is added; for example, amylamine. We have then the case of a solution L_2 containing a little amylamine sulphate with a large excess of H_2SO_4 . The electro-capillary curve of L_2 may be confused with that of L_1 for the positive branch, but separates on approaching the maximum, and remains below for the negative branch.

Ammoniacal Cupric Oxide.—M. Bouzat.—The author determines the heat of formation of ammoniacal cupric oxide and its heat of neutralisation by various acids, and he finds (1) that the ammoniacal cupric base is formed from cupric hydrate and ammonia, with a slight evolution of heat; (2) that this base is a very strong one, much stronger than ammonia, this latter fact being verified by the phenomena of displacement in which it takes part.

Action of Monochlorated Ethyl Acetylacetate on the Diazoic Chlorides.—G. Favrel.—Monochlorated ethyl acetylacetate reacts on the diazoic chlorides in the same way as ethyl methylacetylacetate and ethyl ethylacetylacetate. Elimination of the acetyl group takes place, and formation of hydrazones, in the composition of which the substituted radical (which is in this

case chlorine) is joined to the hydrogen atom of the acetylacetic ether. Using the same method it is found that bodies having the composition of hydrazones derived from ethyl chloroxalate can be obtained. The author proposes to continue his research on the properties of this body.

Certain Salts of Benzylamine.—René Dhommée.—The author prepares a number of salts of benzylamine, the chief being—Benzylaminenitrate, $C_6H_5-CH_2NH_2 \cdot NO_3H$; the acid sulphate, $C_6H_5-CH_2NH_2 \cdot SO_4H_2$; the borate, $(C_6H_5-CH_2NH_2 \cdot 2B_2O_3)_2 + 3H_2O$; the neutral chromate, $(C_6H_5-CH_2NH_2)_2 \cdot CrO_3 + 2H_2O$; the neutral oxalate, $(C_6H_5-CH_2NH_2)_2 \cdot C_2O_4H_2$; the benzoate,—
 $C_6H_5-CH_2NH_2 \cdot C_6H_5-CO_2H$.

MISCELLANEOUS.

Chemical Handicraft.—We have received from Messrs. John J. Griffin and Sons a copy of their new 1902 Catalogue. The firm has spared no pains or expense to make the book as complete as possible; it is profusely illustrated, and includes many new pieces of apparatus.

The Solubility of Salts; Telluric and Allotelluric Acids.—J. Mylius.—The author compares first the hydrates of tellurate of sodium, $TeO_4Na_2 + 2H_2O$ and $4H_2O$, with the corresponding molybdates, chromates, &c.; the first occurs in hexagonal plates soluble in 130 parts of water at 18° , and in 50 parts of water at 100° ; the solutions have a very alkaline reaction, and are precipitated by carbonic acid; the second hydrate is less stable, and is soluble at 18° in 70 parts of water, and at 50° in 40 parts. There also exists a basic tellurate, $TeO_5Na_4 + 8H_2O$. Felted needles form in the presence of an excess of concentrated soda; they are hydrolysed by pure water regenerating the neutral salt. There is also to be obtained a basic lithium salt, $TeO_5Li_4 + 4H_2O$, but no defined neutral one. On examining the solubility of free telluric acid the author gives the curves relating to the different hydrates, $TeO_4H_2 + 6H_2O$ and $2H_2O$, which cross at about $+10^\circ$; he then considers the total or partial dehydration of these hydrates by heat. The most stable hydrate, $TeO_4H_2 + 2H_2O$ or $Te(OH)_6$, calcined at 350° , gives, as is well known, the insoluble yellow anhydride, TeO_3 ; but if heated only to 140° it undergoes aqueous fusion, giving a syrup in which a white, amorphous, granular material is gradually deposited, which only re-dissolves in water with difficulty, and not then regenerating ordinary telluric acid. The solutions of this product differs again from those of TeO_4H_2 by their more distinctly acid taste, their precipitation by alkalis and by carbonate of guanidine, and their electric conductivity. The author admits the existence of a polymer $(TeO_4H_2)_n$, comparable to metaphosphoric acid, and gives it the name *allotelluric acid*. Finally, he observes that persons who have absorbed a small quantity of tellurium (even 1 m.grm. only) are troubled with a metallic taste which persists in the mouth for several days, and at the same time their breath acquires a penetrating odour of garlic; these facts are probably due to the formation of telluride of methyl in the organism.—*Berichte*, vol. xxxiv., p. 2608.

EAST LONDON TECHNICAL COLLEGE. MILE END ROAD, E.

THE DRAPERS' COMPANY will award, on the result of a competitive Examination to be held at the College on the 2nd and 3rd of JULY, 1902, two SCHOLARSHIPS, each of the value of £40, and tenable in the Day Classes of the College for two years; the holder will receive £20 on account of the Scholarship each year, and will be exempt from class fees. Scholarships may be renewed in special cases for a third year.

Candidates must be between 16 and 18 years of age on the 1st of September, 1902.

Entry forms and full particulars may be obtained on application to the Director of Studies, East London Technical College, Mile End Road, E.

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THE CHEMICAL NEWS, JANUARY 23, 1903.

THE
CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXXVI.—1902.

LONDON :

*PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,
E.C.*

AND SOLD BY ALL BOOKSELLERS.

MDCCCII.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,
16, NEWCASTLE STREET, FARRINGDON STREET,
E.C.

THE CHEMICAL NEWS.

VOLUME LXXXVI.

EDITED BY SIR WILLIAM CROOKES, F.R.S., &c.

No. 2223.—JULY 4, 1902.

THE COMPOSITION OF COLOSTRUM.

By WALTER F. SUTHERST, Ph.D., A.I.C.

COLOSTRUM, or biestings, is the fluid secreted by the cow during the time from which she becomes dry to calving, and shows very great difference to ordinary milk in its composition, being much richer in albumenoids and poorer in milk-sugar and fat. In colour it is generally reddish yellow, due chiefly to blood corpuscles; the colour soon passing to the yellow colour of ordinary milk. On heating, it coagulates to a thick jelly-like mass, due to the large amount of coagulable albumenoids present, viz., globulin and albumin. In its chemical composition it differs chiefly from ordinary milk in the amount of globulin it contains, varying in amount from 5 to 18 per cent in the first milking, while milk contains from 0.01 to 0.2 per cent. Previously the albumin and globulin were estimated together, but since more exact methods for their separation have been found, it is as well to estimate both. The amount of albumin is small in comparison with the misleading figures of albumin + globulin previously given, as albumin varying from 0.0 to 2.0 per cent and the casein is not proportionately in such large quantities, varying from 2.75 to 5.35 per cent. The fat varies from 2 to 4.5 per cent, but soon regains its normal amount; the milk sugar is usually present in about the same quantities as the fat, and increases at about the same rate.

Since few complete analyses have been recently carried out with colostrum, the following investigation will no doubt add to the present knowledge of the composition of colostrum. The analyses were carried out in the laboratories of the Cheshire Agricultural College, Holmes Chapel, the colostrum being taken from a shorthorn cow—which calved on April 10, 1902, at 4 p.m.—twice a day, at 6 a.m. and 4.30 p.m. The following were determined in each sample:—

Specific gravity, dry-matter, ash, fat, milk-sugar, total nitrogen, casein, globulin, and the albumin.

The separation of the various albumenoids is the most difficult and usually the most unsatisfactory from a purely chemical standpoint, since the only method available is fractional precipitation, and whether one is always able to completely get rid of the one before precipitating the other is an open question, and possibly the reason of such varied results by different investigators. Still, as most mixtures of albumenoids have been isolated by these means, and shown by ultimate analysis to be very different from each other, one may as well keep to the usual and (at present) only means of separation. An exhaustive investigation into the different methods of separating and determining

the albumenoids of milk has just been published by Gustav Simon (Dissertation, Halle), and from his research the methods giving the most correct results were adopted in the present investigation.

The specific gravity was determined by the pycnometer. For the total solids, 10 grms. of the sample were weighed into a platinum dish, and, after the addition of a few drops of alcohol to cause coagulation, evaporated on the water-bath to dryness, and then dried to constant weight in the hot-air oven at 105° C. The dried mass was carefully heated over a small flame till it had acquired a bright grey colour, and the residue weighed as ash.

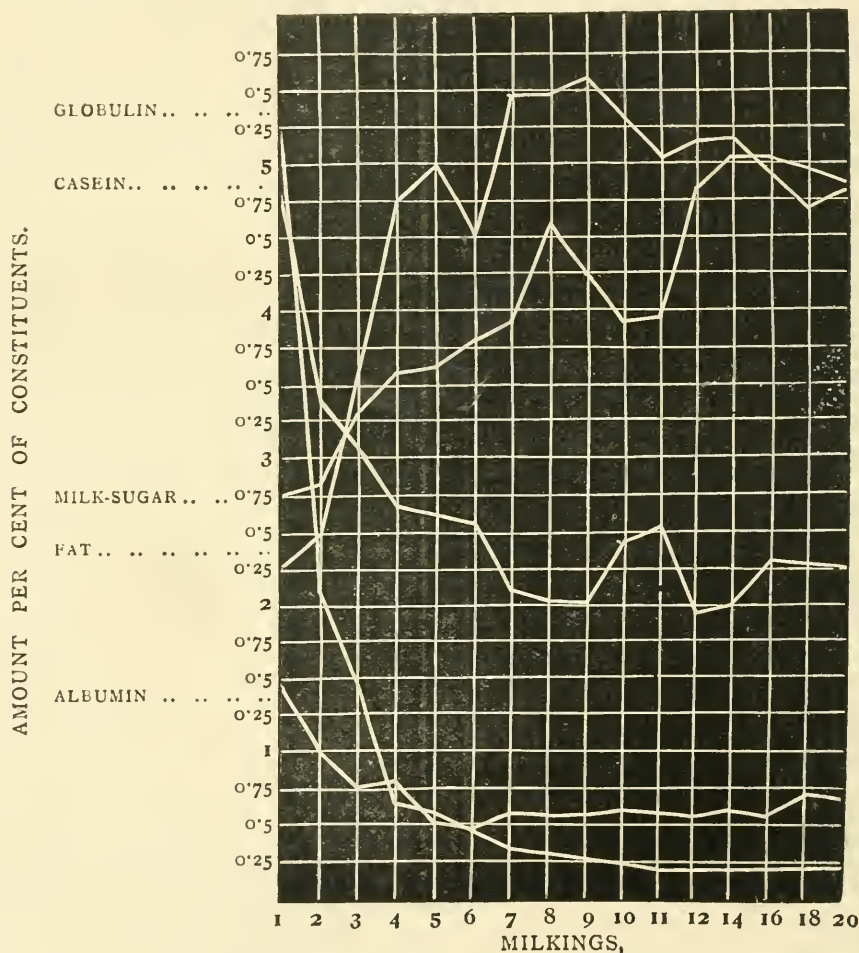
The fat was estimated by Adam's method, using 10 grms. of milk in each case.

For the milk-sugar, 25 grms. were diluted to about 400 c.c. in a 500 c.c. flask, and the albumenoids precipitated by Ritthausen's method, by adding 10 c.c. of Fehling's copper sulphate solution and enough 10 per cent sodium hydrate solution so that the solution still remained slightly acid (usually 7 c.c.). After settling, 100 c.c. of the clear liquid were then run into 50 c.c. of boiling Fehling's solution and boiled for about five minutes. The reduced cuprous oxide was then filtered through an Allihn's filter-tube, dried and reduced in a current of hydrogen, and weighed. From this the milk-sugar was calculated.

The three albumenoids were determined by diluting down 10 grms. of the colostrum to 100 c.c. with water; this being necessary, especially in the first few samples, in order to bring into solution the fairly large amount of suspended albumin. For the precipitation of the casein there are several methods recommended, but the one giving the best results is that of Schlossmann, who uses a saturated solution of alum, since an excess of this reagent does not re-dissolve to any extent the casein. To the diluted colostrum, warmed to 40° C., were added, drop by drop under continued shaking, the alum solution until a flocculent precipitate came down. After cooling, the precipitate was filtered off and washed with distilled water, and the nitrogen estimated by Kjeldahl's process, and the result multiplied by the factor 6.37 taken as casein.

The filtrate was saturated with moistened magnesium sulphate crystals, the precipitated globulin filtered off, and, after washing with saturated magnesium sulphate solution, the nitrogen was estimated. The albumin in the filtrate was precipitated by Almén's tannic acid solution, viz., 4 grms. tannic acid, 8 c.c. 25 per cent acetic acid, and 100 c.c. 45 per cent alcohol. Of this solution, 15 c.c. were used each time, and the nitrogen estimated in the precipitate in the usual way. (In each case the amount of nitrogen contained in the filter-paper used was deducted).

No. of milking.	Dry matter.	Ash.	Fat.	Lactose.	Total albumin.	Casein.	Globulin.	Albumin.	Spec. grav.
1.	22.878	1.034	2.302	2.742	12.236	4.858	5.3206	1.454	1.068
2.	16.232	0.874	2.490	2.852	6.976	3.353	2.048	1.014	1.037
3.	15.158	0.866	3.410	3.376	5.829	3.099	1.451	0.758	1.035
4.	15.902	0.824	4.748	3.628	4.652	2.705	0.662	0.782	1.030
5.	15.738	0.820	5.102	3.636	4.018	2.618	0.558	0.524	1.030
6.	15.748	0.818	4.554	3.862	4.042	2.5631	0.488	0.499	1.029
7.	15.718	0.804	5.496	3.922	3.464	2.211	0.316	0.627	1.029
8.	15.624	0.802	5.470	4.576	3.360	2.176	0.272	0.610	1.030
9.	15.476	0.824	5.626	4.220	3.354	2.150	0.255	0.591	1.030
10.	16.016	0.860	5.372	3.782	3.480	2.427	0.246	0.620	1.031
11.	15.970	0.846	5.048	3.820	3.524	2.520	0.2203	0.597	1.031
12.	16.102	0.842	5.152	4.800	3.062	1.965	0.212	0.554	1.031
14.	16.550	0.844	5.156	5.008	3.216	2.201	0.203	0.562	1.031
16.	16.282	0.836	4.902	5.010	3.328	2.341	0.194	0.554	1.031
18.	16.094	0.820	4.703	4.902	3.314	2.322	0.194	0.571	1.031
20.	16.058	0.814	4.796	4.874	3.242	2.250	0.198	0.562	1.030



For the total nitrogen 5 grms. of the colostrum were taken. The results are given in the accompanying table.

The gradual rise and fall of some of the constituents is strikingly shown by the diagram. In this diagram it is seen that the globulin falls very rapidly for the first few milkings, then soon reaches a constant amount. The quantity of globulin in the later sample does not agree with the figures given by Fleischmann for milk ("Lehrbuch der Milchwirtschaft," p. 30), but as in every case a

fairly large precipitate was obtained with magnesium sulphate, I must stand by the results obtained. It will be seen that the fat and milk-sugar increase, while all the albumenoids decrease; the rise and fall respectively of the milk-sugar and casein corresponding with remarkable exactness.

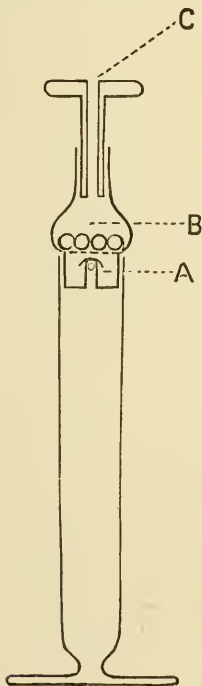
Equilibrium appears to be reached after the ninth milking, and for ordinary purposes the milk could be used after this period.

AN APPARATUS FOR THE DETECTION AND DETERMINATION OF MINUTE TRACES OF ARSENIC.

By EDWIN DOWZARD, F.C.S.

THE accompanying sketch (half actual size) is that of an apparatus for the detection of minute quantities of arsenic.

Using this apparatus $1/10,000,000$ grm. can be detected, and $1/15,000,000$ to $1/20,000,000$ grm. can just be recognised. For all practical purposes $1/4,000,000$ grm. may be taken as the limit. The apparatus is used as follows:—A rod of pure zinc, 2 c.m. long and 5 m.m. in diameter, is placed for about half to one minute in boiling water containing about 5 per cent pure HCl (sp. gr. 1.124); this is to remove any surface impurities. The rod is then washed in distilled water, and placed in the apparatus.



A, Trap.
B, Scrubbing chamber containing beads.
C, Orifice, 3 m.m. in diameter.

Two c.c. of HCl (sp. gr. 1.124), free from arsenic, and containing 6 drops of a 15 per cent solution of cuprous chloride in 100 c.c., is mixed with the substance to be tested, which must be in solution, and the liquid made up to 8 c.c. Before introducing the liquid a piece of Swedish filter-paper, 3 c.m. square, is prepared as follows:—A ring about 12 m.m. in diameter is drawn with a graphite pencil in the centre of paper, which is then moistened inside the ring with 5 per cent mercuric chloride solution, and dried. The ring is drawn merely to show the position of the mercuric spot. The glass beads in the scrubbing chamber may be moistened with a solution of lead acetate or cuprous chloride; the trap underneath is to prevent any washing liquid from entering apparatus, or the scrubbing chamber may be filled with cotton-wool which has been saturated with a 5 per cent solution of lead acetate, and dried.

The mercuric chloride paper is now attached to the top of apparatus with a clip, so that the orifice is under the centre of ring. The liquid to be tested is introduced into apparatus, which is placed in water at 60°C . (the water

should be on the same level as the liquid inside apparatus). After thirty minutes the paper is removed and examined in full daylight; a minute trace is indicated by a lemon-yellow spot and a trace by a deep orange-brown spot.

A blank test with the reagents must precede the examination. It is only necessary to test the same batch of acid and zinc occasionally.

In the absence of organic matter this test is of extraordinary delicacy; for instance, if the sample is a liquid and 4 c.c. is used, 1 part in 16,000,000 can be detected. If the sample is a solid and 0.5 grm. is used, 1 part in 2,000,000 can be detected.

Organic substances and liquids containing organic substances should be treated as follows:—

Solids.—0.5 grm. is made into a paste or strong solution with water, and mixed with 0.2 grm. of pure calcium oxide free from arsenic; the mixture is then dried on an asbestos felt and ignited; this should be done in a small porcelain dish. The residue is mixed with a few c.c. of water, and HCl added drop by drop until solution is effected; this solution is then examined as described above.

Liquids.—Two c.c. is mixed with 0.1 grm. of pure calcium oxide free from arsenic, and the mixture treated as in the case of solids.

If the sample to be examined contains sulphites or hypophosphites it should be treated as follows:—The substance should be dissolved in water or dilute HCl, a slight excess of bromine water added, and the mixture heated until free from bromine; the solution is then cooled, and treated as before described. This apparatus is recommended for the examination of beer and glucose for arsenic; the lime treatment should be followed. To facilitate comparisons with the standards, the yellow spots should be encircled with a black band about 2 m.m. wide, made with a graphite pencil; the inner edge of the band should touch the outer edge of the spot.

In the quantitative determination of minute traces of arsenic by this method the following points should be observed:—

1. The amount of HCl used, the final bulk of the liquid, and the size of the zinc rod should always be the same. The starting temperature should be 60°C .
2. The reaction should always occupy thirty minutes.
3. When comparing the sample with known amounts of arsenious acid; the standard test must contain the same weight or volume of the same substance as sample, but free from arsenic.

A standard set of spots may be prepared for each substance; they should be kept in a tightly stoppered bottle in a dark dry place.

The cuprous chloride solution is prepared as follows:—Sixteen grms. of pure CuO are dissolved in 110 c.c. of HCl, 13 grms. of thin copper-foil are cut into small pieces, and boiled with the above solution for twenty-five minutes; the resulting solution of cuprous chloride is poured into 1000 c.c. of distilled water, and the white precipitate washed by decantation. The chloride is then dissolved in HCl free from arsenic, and the solution standardised to contain about 15 grms. of cuprous chloride in 100 c.c.

The apparatus described above is made by Messrs. Gallenkamp and Co. 19, Sun Street, London.

A Method for the Volumetric Estimation of Silver.—L. W. Andrews.—To the solution containing the silver to be estimated, slightly acidulated with nitric acid, a ferrous as well as a ferric salt is added; at least as much iron in each of these two salts as there is silver to estimate. Then, by means of a graduated burette, a titrated solution of iodine is added, coloured blue with starch; this solution should be added gradually with frequent stirring. The burette is read off at the moment when the colouration persists. The reaction is as follows:— $2\text{NO}_3\text{Ag} + 2(\text{NO}_3)_2\text{Fe} + \text{I}_2 = 2\text{AgI} + (\text{NO}_3)_3\text{Fe}_2$. — *Zeit. Anorg. Chem.*, vol. xxvi, p. 175.

DOUBLE SALTS IN SOLUTION.

By P. N. EVANS.

THE writer's attention was recently called to the fact that some electrolytes in saturated aqueous solution are not precipitated by the addition of a second electrolyte having an ion in common with the first. As on further investigation several instances of this kind were noted, an explanation was sought; some of the facts have been observed by others, but no attempt made to account for them. A reasonable solution of the difficulty is, it is thought, here presented.

The case may be briefly stated as follows:—When an electrolyte capable of dissociating into two ions is dissolved in water, the proportions existing between the ionised and non-ionised molecules is supposed to be represented, according to Van der Waal's equation, by the expression $a.b = k.c$, in which a , b , and c are the concentrations of the anions, kathions, and non-ionised molecules of the electrolyte respectively, and k a constant depending on the nature of the electrolyte, and independent of the concentration for moderately or highly dilute solutions.

Supposing this equilibrium to have become established, which is the case in an exceedingly brief time, if not instantaneously, any addition of either kind of ion concerned, the quantity of solvent remaining the same, must result in an increased value for its concentration, and produce a corresponding increase in the number and concentration of the non-ionised molecules; for, k being a constant, any increase in the value of a or b will involve an increase in that of c if the equilibrium is to be maintained.

If to a saturated solution of an electrolyte there be added a second soluble electrolyte having an anion or a kathion in common with the first, there must result a state of supersaturation with regard to the first electrolyte or a separation of a portion of it in solid form.

Many examples of this are familiar to all chemists. For instance, a saturated solution of sodium chloride is instantly precipitated by the addition of concentrated hydrochloric acid, in spite of the water that is added at the same time; this case is complicated and the precipitation assisted by the chemical union taking place between the hydrochloric acid and some of the water, made evident by the evolution of heat, thus increasing all the concentrations by removing (chemically changing) some of the solvent. The same result is obtained and the same reasoning applies when calcium chloride is added to a saturated solution of sodium chloride. The precipitation of sodium chloride is brought about without this complication of causes by the addition of crystallised potassium chloride and by anhydrous sodium sulphate, and even crystallised sodium sulphate, ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), gives the same result in spite of the water added in the crystals.

Similarly, potassium chloride can be precipitated by hydrochloric acid (HCl), sodium chloride (NaCl), or potassium sulphate (K_2SO_4); and copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) by cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), or sulphuric acid (H_2SO_4); barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) by hydrochloric acid or sodium chloride; calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) by sulphuric acid, potassium sulphate, calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$); lead chloride (PbCl_2) by hydrochloric acid, sodium chloride, potassium chloride.

In this list we have a very wide range of solubility:—100 parts of water dissolve NaCl , 35; KCl , 32; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 40; $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, 33; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.20; PbCl_2 , 0.74 parts. It is not evident whether easily or difficultly soluble substances should respond more readily in yielding a precipitate under these conditions, for the much greater degree of supersaturation attainable with an easily soluble substance, provided precipitation does not take place, may be offset by the greater difficulty in disturbing this state of supersaturation and causing the separation of a solid.

The greater the solubility of the electrolyte added to

the saturated solution, the more readily a precipitate should be obtained; and the higher the ionisation constant of the second electrolyte, the more probable is a marked result.

In spite of the apparently favourable conditions in this respect, all attempts to precipitate lead chloride from its saturated solution by means of lead nitrate were fruitless. A saturated solution of the chloride is very easily prepared, owing to the great difference in solubility in hot and in cold water, by warming the solution in contact with an excess of the salt, and then cooling and decanting. The immediate and copious precipitate produced in this solution by the addition of sodium or potassium chloride or hydrochloric acid seems to indicate that the tendency to remain in the supersaturated condition is very slight in the case of this salt, yet the addition of lead nitrate crystals ($\text{Pb}(\text{NO}_3)_2$) to the solution, even in the quantity made possible by the ready solubility of the nitrate (48 parts in 100), fails to cause any precipitation, either immediately or on long standing, or even on adding a crystal of lead chloride to induce crystallisation from the solution, supposing it to be supersaturated. Lead nitrate, like most normal salts, has a high ionisation constant, more than half that of the strongest acids in a 0.1 per cent solution—calculated by Arrhenius from conductivity experiments by Kohlrausch. This fact, and its ready solubility, should be most favourable to the precipitation of the lead chloride, on account of the considerable increase in the concentration of the lead ions made possible thereby.

In harmony with the usual similarity of barium to lead, a saturated solution of barium chloride shows no sign of precipitation with barium nitrate ($\text{Ba}(\text{NO}_3)_2$); as already stated, a precipitate is produced by the addition of hydrochloric acid, or sodium or potassium chloride, to the saturated barium chloride solution.

Similarly, potassium sulphate, though precipitated from its saturated solution by the addition of potassium chloride or sodium sulphate, gives no precipitate with sulphuric acid; and calcium sulphate is not thrown down by either sodium sulphate or ammonium sulphate, but does separate slowly on the addition of potassium sulphate, and more quickly with sulphuric acid.

Apparently, then, in these cases, the number of non-ionised molecules of the first is not increased by the addition of the second electrolyte, and the only plausible explanation seems to be that in these cases double salts are formed, namely, lead chloride-nitrate (PbClNO_3), barium chloride-nitrate (BaClNO_3), hydrogen potassium-sulphate (HKSO_4), calcium-sodium sulphate ($\text{CaNa}_2(\text{SO}_4)_2$), and calcium-ammonium sulphate ($\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2$). The simplest formulæ are here suggested, but of course the proportions of the two acids or two bases in the molecule may not be as represented in these.

Taking the case of lead chloride as an example, the addition of the lead nitrate must immediately increase the number of lead ions, but at the same time diminishes both this and the number of the chlorine ions by permitting the formation of lead chloride-nitrate, so that the value of the product of the concentrations of lead and chlorine ions is not thereby increased, thus causing no rise in value of the concentration of the lead chloride, and therefore no separation of this substance as a precipitate. It does not follow, however, that this peculiarity of behaviour must accompany the formation of a double salt under similar circumstances, for it may be that the increase of the concentration of one kind of ion concerned may more than counterbalance the simultaneous decrease in this and that of the other kind of ion involved; this is simply a question of the ionisation constants of the electrolytes present.

It seems reasonable to suppose that double salts should exist whenever there is a polyvalent acid in presence of two or more bases, or a polyvalent base in presence of two or more acids, though other evidence of the existence of most of these compounds is at present lacking. Since, however, we commonly know and recognise the existence

of only those double salts which separate out from solutions of their constituents rather than these constituents themselves in distinct crystals, the evidence so far accepted for the existence of such compounds is of a very limited kind, namely, only their solubility relative to that of their constituents. In other words, if these separate in preference to the double compound, the latter does not exist so far as this kind of evidence is concerned.

Now supposing that in a solution of equivalent quantities of the constituents, the ionisation constants of these and the double salt are such that approximately equal numbers of molecules of the three kinds exist in the non-ionised condition, and the solution be concentrated, the double salt will separate if its molecular solubility (solubility divided by molecular weight) is less than that of either constituent, but not otherwise. Of course it is not probable that the constants are such as to more than approximately produce a condition like that imagined in the example just described; but inasmuch as normal salts do not differ very widely in their ionisation constants, the facts may be nearly enough in harmony with the supposition to make a study of these molecular solubilities not without interest in this connection, though the data available are not so numerous as desired.

An examination of the solubilities of twelve double salts selected at random shows the facts to be in accordance with this theory without a single exception, namely, that the molecular solubility of the double salt is less than that of either constituent. The figures are given in the following table, the formulæ being those of the substances separating out as crystals from their solutions:—

Formula.	a = molecular weight.	b = sol- ubility in 100 parts water.	b ÷ a = molecular solubility (× 100).
K ₂ SO ₄	174	12.5	7.2
Al ₂ (SO ₄) ₃ .18H ₂ O ..	665	85	12.8
KAl(SO ₄) ₂ .12H ₂ O ..	474	9.5	2.0
(NH ₄) ₂ SO ₄	132	77	57.6
Al ₂ (SO ₄) ₃ .18H ₂ O ..	665	85	12.8
(NH ₄)Al(SO ₄) ₂ .12H ₂ O ..	452	9	2.0
K ₂ SO ₄	174	12.5	7.2
Cr ₂ (SO ₄) ₃ .18H ₂ O ..	717	120	16.7
KCr(SO ₄) ₂ .12H ₂ O ..	500	20	4.0
(NH ₄) ₂ SO ₄	132	77	57.6
Cr ₂ (SO ₄) ₃ .18H ₂ O ..	717	120	16.7
(NH ₄)Cr(SO ₄) ₂ .12H ₂ O ..	478	over 12	over 2.5
K ₂ SO ₄	174	12.5	7.2
Fe ₂ (SO ₄) ₃ .9H ₂ O ..	562	over 80	over 14.1
KFe(SO ₄) ₂ .12H ₂ O ..	503	20	4.0
(NH ₄) ₂ SO ₄	132	77	57.6
FeSO ₄ .7H ₂ O	278	60	21.6
(NH ₄) ₂ Fe(SO ₄) ₂ .6H ₂ O ..	392	17	4.3
NH ₄ Cl	53.4	33	61.8
SnCl ₄ .5H ₂ O	350	over 1900	over 543
(NH ₄) ₂ SnCl ₆	366	33	9.0
K ₂ SO ₄	174	12.5	7.2
CaSO ₄ .2H ₂ O	172	0.205	0.12
CaK ₂ (SO ₄) ₂ .H ₂ O ..	328	0.25	0.08
K ₂ SO ₄	174	12.5	7.2
CoSO ₄ .7H ₂ O	280	58	20.7
K ₂ Co(SO ₄) ₂ .6H ₂ O ..	437	19	4.3
K ₂ SO ₄	174	12.5	7.2
NiSO ₄ .7H ₂ O	281	67	23.9
K ₂ Ni(SO ₄) ₂ .6H ₂ O ..	437	5.3	1.2
KCl	75	32	42.6
MgCl ₂ .6H ₂ O	203	130	64.0
KMgCl ₃ .6H ₂ O	278	64.5	23.2
K ₂ CO ₃	138	110	80.0
Na ₂ CO ₃ .10H ₂ O	286	21	7.3
KN ₂ CO ₃ .6H ₂ O	230	13	5.6

Purdue University, Lafayette, Indiana, U.S.A.,
April, 1900.

ON THE RELATIONS OF SULPHUR AND IODINE, AND THE IODIDES OF SULPHUR.

By R. W. EMERSON MACIVOR, F.I.C., &c,
Formerly Assistant Professor of Chemistry, Anderson's College
(Medical Faculty), Glasgow, &c.

OUR knowledge of the relations of sulphur and iodine, and of the so-called iodides of sulphur, is in a somewhat confused state. In many of our text-books we read that the blackish-grey indistinctly crystalline body formed when a mixture of the elements in equal atomic proportions is heated, even under water, is the mono-iodide, S₂I₂. Now, as a matter of fact, this product entirely lacks the chemical characteristics which analogy with the chloride and bromide indicates would be possessed by a true iodide. Gay-Lussac in 1813 (*Ann. de Chim. et de Phys.*, lxxxviii., 308) states that any union between sulphur and iodine must be of the most feeble kind; indeed, that doubt might be placed on the possibility of two bodies so akin in nature and properties entering into true chemical combination at all. I hope to show that the bulk of evidence to date fully endorses the view thus expressed over ninety years ago.

The melting-point of the "blackish-grey material"—which, by the way, is 66°, and not 60° as given in the text-books—being so much below that of either of the elements composing it is the only strong fact in favour of its being a true chemical combination, but, remarkable to say, in all its other properties it more resembles a mixture formed by the solution, or may be partial solution, according to circumstances, of the one element in the other, and the slight evolution of heat which is said (but never yet proved) to take place when the act of union occurs might be attributable to this process of mere solution no less than to actual chemical combination.

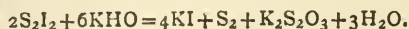
It is now some twenty-eight years since I sent a communication on the subject of iodide of sulphur to the CHEMICAL NEWS (vol. xxx., p. 179), in which I gave the results of some experiments which had led me to doubt the compound nature of the product formed by simply melting a mixture of sulphur and iodine. I particularly noted that not only did the material readily yield up the whole of its iodine to such solvents as alcohol (preferably containing some ethyl iodide to increase the solvent power of the spirit) and a solution of potassium iodide, but that the sulphur left behind was in a crystalline form, and therefore readily soluble in carbon disulphide. To this latter fact I at the time attached some importance, it having been shown long before by Berthelot that sulphur separated from compounds, such as S₂Cl₂, wherein it acts as the positive radicle, is not soluble in the disulphide.

Later experiments, carried out at irregular periods and in widely different places, have more than confirmed the impression made on my mind so long ago, viz., that no definite iodide of sulphur is formed when a mixture of sulphur and iodine is simply heated to fusion. In all my efforts to form S₂I₂ in this way I exercised the utmost care in regulating the temperature at which the process of fusion was effected so as to keep it as low as possible, and thereby prevent the dissociation of any iodide that might be formed. The product obtained, however, when dissolved in CS₂ invariably gave a solution which on slow evaporation yielded successive crops of crystals containing variable percentages of sulphur. Thus in one series of operations I obtained the following results:—

First crop of crystals contained	0.38	per cent S
Second " " "	1.09	"
Third " " "	3.51	"
Fourth " " "	38.56	"

The final residue left after the evaporation of the solvent contained about 80 per cent of sulphur. When digested in KHO or NaHO the substance gave up the whole of its iodine, leaving all the sulphur behind in rhombic form, and no sulphite or thiosulphates were found in the solu-

tion, as would assuredly been the case had any S_2I_2 been present:—



The efforts made by chemists in different countries to form definite iodides of sulphur by bringing the constituent elements into close molecular association by mixing their carbon disulphide solutions have led to most contradictory results. Lamers (*Fourn. Prakt. Chem.*, 1861, lxxxix., 349) obtained "what he believed to be sulphur hexaiodide, SI_6 , in the following manner:—Solutions of sulphur and iodine in various proportions in carbon disulphide were allowed to gradually evaporate at low temperatures, when crystals of the compound invariably separated out, no matter what the relative proportions of the two elements in the solution had been; unless, indeed, one or other of them, being in great excess, separated first before the hexaiodide crystallised out." G. vom Rath (*Pogg. Ann.*, cx., 17) submitted some crystals of the supposed new iodide to crystallographic examination, and was disposed to regard them as being isomorphous mixtures of sulphur and iodine, only he thought these elements were from his standpoint too dissimilar to form such mixtures. McLeod (*Brit. Assoc. Reports*, 1892, p. 690), and several other authorities, including Linebarger (*Amer. Chem. Journ.*, xvii., 33–59), have, however, clearly shown that the supposed SI_6 obtained by Lamers is merely a mixture of the two elements. In several trials made on the lines of Lamers' work I also failed to form the compound. Schlagdenhauffen (*L'Union Pharmaceutique*, civ., 1874) says:—"When solutions of sulphur and iodine in carbon disulphide are mixed, a coloured solution is obtained no matter what the relative quantities of the two elements may be; no heat is evolved, hence no action—no combination; it is a simple mixture of the metalloids." In this connection it is noteworthy that Ogier (*Comptes Rendus*, 1881, xcii., 9, 22) determined the heat of combination and of solution in carbon disulphide of a compound of sulphur and iodine, "which was stated to be S_2I_2 , and to have the character of a definite body"; he found the first to be quite too small to be taken into account, and the second to be equal to the sum of the heats of the two elements alone in the solvent. Linebarger (*Amer. Chem. Journ.*, xvii., 33–59) points out that Ogier does not indicate the degree of concentration of the solutions of sulphur and iodine which he mixed, and therefore the only legitimate conclusion to be drawn from his statements is that in dilute solutions no combination between the elements takes place. Working with concentrated solutions containing sulphur and iodine in equal atomic proportions he obtained by fractional crystallisations four crops of crystals, each of which on analysis proved to have the composition S_nI_n . The solutions invariably gave this result, provided the evaporation was carried out very slowly and at a temperature of 10–15°. Linebarger, however, though having no thermo-chemical apparatus at hand, was unable to determine the heat evolved (if any) by the union of the elements in his concentrated solutions so to compare its amount with the sum of the heats of sulphur and iodine separately in the CS_2 . Neither did he make any crystallographic examination of his S_nI_n , but formed the opinion that the crystals were "rhombic tablets more or less pronouncedly." This chemist concludes, after an apparently earnest and painstaking research, that there is only one definite compound of sulphur and iodine, and that its molecular weight is S_2I_2 ; its state of combination is very weak, and the elements seem to be in a condition of molecular rather than atomic union:—"There seems to be more tendency on the part of the sulphur and iodine atoms to form molecular aggregations than to combine with each other."

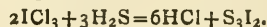
(My efforts to obtain crystals of this mono-iodide, or indeed any other definite iodide, from carbon disulphide solutions—whether concentrated or weak—were not successful. Adopting the system of fractional crystallisation, and taking all precautions with respect to the rate

of evaporation, I found invariably that each succeeding crop of crystals contained more sulphur than its predecessor, until finally a residue consisting chiefly of sulphur remained after the disappearance of the solvent. These results were, of course, in my opinion, due to the fact that the elements were not in actual chemical union in the solution, and that therefore the tendency of the less soluble iodine was to first separate out. A concentrated solution in which the elements were mixed in equal atomic proportions yielded crystals containing:—

First crop of crystals	=	0.42	per cent sulphur
Second	"	"	"
Third	"	"	"
Fourth	"	"	"

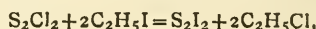
On allowing the mother-liquor to completely evaporate a residue containing over 80 per cent of sulphur remained. Treated with a solution of potassium hydrate, neither the crystals nor the residue yielded a sulphite or thiosulphate, but merely gave up their iodine, leaving behind rhombic sulphur).

Grosourdi, and later Lamers (*Fourn. Prakt. Chem.*, 1861, lxxxiv., 349) state that an iodide of sulphur having approximately the formula S_3I_2 is obtained as a reddish-brown amorphous mass by the action of sulphuretted hydrogen on an aqueous solution of $KCl.ICl_3$:—



I repeated the work of these chemists, and am inclined to think an iodide of sulphur is formed by the interaction of these substances, but if the passage of the gas is sufficiently prolonged, the final products of the reaction are hydrochloric and hydriodic acids and free sulphur. It is, however, interesting to note that much of this sulphur is insoluble in carbon disulphide, which, if we accept the Berthelot theory, would indicate that it had been in the first stage of the reaction in actual chemical union with iodine. The reddish-brown powder quickly loses its iodine on warming *in vacuo*, melts at 66°, and yields some thiosulphate with separation of sulphur when acted upon by a solution of KHO. I hope to deal further with this interesting reaction in a future paper.

F. Guthrie (*Chem. Soc. Journ.*, xiv., p. 57) by acting upon sulphur monochloride with ethyl iodide, preferably in hermetically closed tubes, and in the proportions shown in the equation—



obtained the monoiodide "in the form of fine tabular crystals of the lustre of iodine and in a state of absolute purity." Although the synthesis of the compound would enable one to infer its exact composition, Guthrie, to further satisfy himself, submitted a quantity to analysis by heating in a combustion tube with KNO_3 and Na_2CO_3 , whereby the sulphur and iodine were converted respectively into KI and K_2SO_4 . The results obtained were:—

	Theory.	Found.
S	20.13	20.28
I.. . . .	79.87	79.81
	100.00	100.00

It is much to be regretted that Guthrie did not carry his work further. The method of analysis adopted could throw no light on the true constitution of the crystals. It in no way helped to prove that S_2I_2 had actually been formed in accordance with the equation, and, indeed, later investigation has shown that the sulphur and iodine are liberated in elementary form and crystallised as mere mixtures. McLeod (*Brit. Assoc. Reports*, 1892, p. 690) found the product of the reaction to have more the nature of a non-metallic alloy than a definite iodide, while Snape (*CHEMICAL NEWS*, lxxiv., 27–29) found the crystals, which at first sight appeared homogeneous and dark, on microscopic examination, to consist of a mixture of opaque

iodine and transparent rhombic sulphur crystals, from which he extracted by means of ether the whole of the iodine. On slowly volatilising the iodine from a quantity of the powdered crystals Snape obtained a residue "equivalent to 20.16 per cent of sulphur, theory requiring 20.13," and points out that "whether chemical union has taken place or not, equivalent proportions of the sulphur and iodine necessarily constitute the residue of Guthrie's operations after the expulsion of the ethyl chloride." In preparing some of the crystals, I followed the instructions given by Guthrie in his paper, and found the product to have all the appearances therein stated, but on dissolving it in carbon disulphide and submitting the solution to slow evaporation I obtained successive crops of crystals which showed an irregularity in composition similar to that observed in the case of the product formed by the simple fusion of a mixture of sulphur and iodine. The powdered crystals completely surrendered their iodine to KHO, and in the solution I failed to detect either any sulphite or thiosulphates, while the sulphur left after the removal of the iodine was in the rhombic state.

The opinion expressed by Sestini (*Repertoire de Chimie Appliquée*, 1863, v., 481) may not be so far from the truth after all:—There exist a great number of compounds of sulphur and iodine obtained by fusion and solution, all being analogous in character to metallic alloys." In any case it is high time that the authors of some of our more modern text-books should make their references to the "iodides" of sulphur more in harmony with ascertained fact than they appear to have hitherto done.

In an early communication to the CHEMICAL NEWS I shall give the further results of my investigations, and hope to produce certain physico-chemical data which may make more easily understandable the true relations of sulphur and iodine.

The Laboratory,
29, Fenchurch Street, London, E.C.

ESTIMATION OF THALLIUM IN THE THALLOUS STATE.

By V. THOMAS.

DURING the course of the research I have been carrying on for the last two years on the thalious salts, I have had many occasions to estimate thallium in the thalious state. The method I constantly used consists in transforming the salts of the protoxide into salts of the sesquioxide. It has the advantage of great simplicity over the older methods which have been in use up to the present, besides being much more accurate.

The oxidising agent used is bromide of gold, or, to speak more accurately, bromo-auric acid. By reduction the bromide of gold loses three atoms of bromine, and gives a deposit of metallic gold which can be weighed, so that when the reduction is terminated two atoms of gold correspond to three atoms of thallium, according to the reaction $3\text{TiCl} + 2\text{AuBr}_3 = 3\text{TiClBr}_2 + 2\text{Au}$.

It follows that, taking 197 as the atomic weight of gold and 204 as that of thallium, we can immediately find the amount of thalious thallium existing in combination, by multiplying the weight of the reduced gold by—

$$\frac{3 \times 204}{2 \times 197} = 1.5533.$$

The salt of thallium I used to control this method was the protochloride. So as to obtain it in a satisfactory state of purity the commercial product was washed with cold water several times, then transformed into the trichloride, and finally reduced by means of sulphurous acid. The precipitated chloride was dissolved in boiling water, and the solution left to cool. The chloride thus deposited was then ready for analysis.

A known weight of the chloride, about 0.5 grm., was

dissolved in cold water. The solution was heated on the water-bath, and the solution of bromide of gold added. The reduction takes place immediately, or at the end of a few moments. The gold is precipitated in the form of a brown powder, which sometimes, but rarely, has a metallic lustre. After making certain that the amount of bromide of gold added is sufficient, which can be seen immediately by the colour of the solution, the whole is left in a warm place for eight or ten hours; the gold is then collected on a filter, dried, and weighed.

In this manner I found the proportion of thallium in the protochloride to be:—

I.	II.	III.	IV.	V.	Theory.
Tl = 85.02	85.29	85.16	85.30	85.18	85.21

These figures all agree within 0.25 per cent.

When the estimation has to be carried out on very small quantities the figures come out a little too high. In such a case, the amount of gold weighed being very small, it is probable that the gold reduced by the fumes in the laboratory during the time the solution is left to stand in a warm place, comes into account, although the amount is very small. I obtained the following results:—

TiCl taken.	Gold weighed.	Tl found.	Tl calculated.
0.2320	0.1280	85.69	85.21
0.2940	0.1620	85.58	—

Practically at least 0.2 or 0.3 grm. of gold should be weighed to obtain good results.

The bromo-auric acid used was prepared very easily by dissolving gold in bromised bromhydric acid. After solution it is evaporated on the water bath.

The bromo-auric acid is then deposited on cooling in long dark coloured needles, which are easily re-dissolved in water. The filtered solution is kept ready for use. When we use solutions which have been prepared for some time it is necessary to make certain that they are perfectly clear.

It often happens that after a long time solutions of bromide of gold deposit a yellowish-brown powder on account of a slight reduction which takes place. This powder, if we are not careful, may remain in suspension for a considerable time and remain unnoticed; it is therefore advisable to use solutions which have been recently filtered.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 11.

ON THE DOUBLE SALTS OF TETRATOMIC TITANIUM.

By A. ROSENHEIM and C. SCHÜTTE.

I. Chlorotitanic Acid.

RECENTLY distilled chloride, TiCl_4 , dissolves in well-cooled fuming hydrochloric acid, giving a deep yellow solution which undoubtedly contains TiCl_6H_2 , but this product has not yet been isolated. When treated with cold water the solution remains limpid for some time, and finally deposits gelatinous titanic acid. The same takes place with a solution of this latter substance in fuming nitric acid. $\text{Ti}(\text{OH})_4$ has also been added to a solution of hydrochloric acid gas in absolute alcohol or ether, both being kept thoroughly well cooled; the reaction is very brisk. These solutions were then kept boiling for two or three hours in a flask fitted with a vertical condenser; the very titaniferous filtered liquors were then evaporated to dryness under reduced pressure, and a very refrangible, deep yellow coloured oily liquid was obtained, undoubtedly containing TiCl_6H_2 , but it could not be isolated, as the product of the ethyliferous residue decomposed when an attempt was made to distil it *in vacuo*.

During its preparation, a yellowish-white precipitate was also formed by the action of $\text{Ti}(\text{OH})_4$ on the

hydrochloric acid in the ether; its composition was $\text{TiCl}_3\text{OH} + (\text{C}_2\text{H}_5)_2\text{O}$.

Chlorotitanate of Ammonium, $\text{TiCl}_6(\text{NH}_4)_2 + 2\text{H}_2\text{O}$.—Solid chloride of ammonium is added to the hydrochloric solution of TiCl_3 ; this is thoroughly stirred while being kept quite cold. At the end of twelve hours a slightly crystalline, bright yellow deposit is formed, which is washed with ether. This salt is very easily decomposed in moist air, and becomes white.

In the same manner we obtain the *chlorotitanate of pyridine*, $\text{TiCl}_6\text{H}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, in small yellow crystals, but this is prepared by using an alcoholic solution; the salts of *quinoline*, $\text{TiCl}_6\text{H}_2 \cdot 2\text{C}_9\text{H}_7\text{N}$, and of *aniline*, $\text{TiCl}_6\text{H}_4 \cdot 4\text{C}_6\text{H}_5\text{NH}_2$, are prepared in a similar manner.

Ammoniacal Tetrachloride of Titanium, $\text{TiCl}_4 \cdot 4\text{NH}_3$.—This is an amorphous powder of a deep-yellow to reddish-brown colour, and is precipitated when we pass a current of ammonia gas through a concentrated and well cooled solution of TiCl_4 in perfectly anhydrous ether. In the same way with *pyridine* in ethereal solution we get an analogous body, $\text{TiCl}_4 \cdot 6\text{C}_5\text{H}_5\text{N}$.

II. Bromotitanic Acid.

Bromide of titanium gives results similar to those furnished by TiCl_4 ; by reacting on an alcoholic solution of hydrobromic acid, the concentrated solution deposits a white crystalline powder consisting of $\text{TiBr}(\text{OH})_3 + \frac{1}{2}\text{H}_2\text{O}$. Under the same conditions as with chlorotitanate of ammonium we obtain a *bromotitanate of ammonium*, $\text{TiBr}_6(\text{NH}_4)_2 + 2\text{H}_2\text{O}$, in almost black, red crystals. With bromohydrate of pyridine in the presence of an excess of hydrobromic acid, in alcoholic solution, we obtain the *bromotitanate of pyridine* in crystals of the same colour, and having a metallic lustre; but if the acid is not in excess we obtain, on evaporation in the cold, yellow needles of $\text{TiOBr}_2 \cdot 3(\text{C}_5\text{H}_5\text{N} \cdot \text{HBr})$. Finally, ammonia-gas, passed through an ethereal solution of TiBr_4 , gives a brown amorphous body which is without doubt $\text{TiBr}_4 \cdot 6\text{NH}_3$.

III. Titanic Thiocyanate.

An ethereal solution of TiCl_4 , well shaken up with thiocyanate of lead and filtered, gives on evaporation, first of all yellow needles which are probably persulphocyanic acid, then very deep reddish-brown needles having a metallic lustre; these cannot be re-dissolved without decomposition, and the formation of persulphocyanic acid, &c.; it is doubtless a titan polythiocyanate. $\text{Ti}(\text{OH})_4$ dissolves readily in an aqueous solution of CNSH, giving a red colouration.

IV. Sulphates of Titanium.

Titanic hydrate can be dissolved in a warm alcoholic solution of sulphuric acid, and the evaporated liquid gives a white amorphous deposit of *basic titan sulphate*, $\text{SO}_4\text{TiO} + 6\text{H}_2\text{O}$.

A solution of $\text{Ti}(\text{OH})_4$ in concentrated sulphuric acid, being carefully treated with a concentrated aqueous solution of potassic sulphate, gives an abundant crop of needle-shaped crystals felted together; this is the double potassic sulphate, $3\text{SO}_4\text{TiO} \cdot 2\text{SO}_4\text{K}_2 + 10\text{H}_2\text{O}$. In a similar manner we obtain the corresponding ammoniacal salt, $\text{SO}_4\text{TiO} \cdot \text{SO}_4(\text{NH}_4)_2 + \text{H}_2\text{O}$.

V. Oxalates of Titanium.

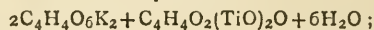
By the evaporation of a solution of $\text{Ti}(\text{OH})_4$ with a solution of binoxalate of potassium or of ammonium we obtain needles which can be re-crystallised in water; they consist of $(\text{C}_2\text{O}_4\text{K}_2)_2\text{TiO} + 2\text{H}_2\text{O}$, and also large clinorhombic crystals of $[\text{C}_2\text{O}_4(\text{NH}_4)_2]_2\text{TiO} + \text{H}_2\text{O}$.

The solution of these salts gives, with just the right quantity of BaCl_2 , a crystalline precipitate of $(\text{C}_2\text{O}_4)_2\text{BaTiO} + 2\text{H}_2\text{O}$. The evaporation of a solution of $\text{Ti}(\text{OH})_4$ in an aqueous solution of $\text{C}_2\text{O}_4\text{H}_2$ does not give any crystals, but in alcoholic solution a white, micro-crystalline product is obtained, soluble in water and in alcohol; this is the *basic oxalate of titanium*, containing

alcohol of crystallisation, $\text{C}_2\text{O}_4\text{TiO} + \text{C}_2\text{H}_5\text{OH}$. In aqueous hydrochloric solution a white amorphous body is obtained, $(\text{C}_2\text{O}_4\text{TiO})_2\text{O} + 12\text{H}_2\text{O}$.

VI. Tartrate of Titanium.

From alkaline bitartrates, after evaporation of the solutions, we obtain a white powder of—



the salts of sodium and of ammonium contain H_2O .

The simple tartrate is $(\text{C}_4\text{H}_6\text{O}_2)_2\text{Ti} + 4\text{H}_2\text{O}$; it is an amorphous mass, soluble in water, $[\alpha]_D = 140^\circ 8'$. In the presence of alcohol we obtain $\text{C}_4\text{H}_4\text{O}_6(\text{TiO})_2\text{O} + 7\text{H}_2\text{O}$, insoluble in water, but soluble in acids and in ammonia.—*Zeit. Anorg. Chem.*, vol. xxvi., p. 239.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, June 5th, 1902.

Prof. THORPE, C.B., F.R.S., Vice-President, in the Chair.

MESSRS. Steel, F. King, S. King, West, and F. M. Perkin were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edgar Leeder Edlin, B.A., Marsh Parade, Newcastle, Staffs; George Felix Dudbridge Green, 9, Ross Road, South Norwood, S.E.; Arthur Francis Hosking, Roskear Villas, Camborne, Cornwall; Douglas K. Jardine, B.Sc., 20, Doune Terrace, Kelvinside, Glasgow; Leonard Smith, 14, West Hill, Highgate, N.

The certificate of Mr. Herbert Purton, London Chambers, Durban, Natal, authorised by the Council under By-law I. (3), was read.

Of the following papers, those marked * were read:—

*91. "The Action of Ungerminated Barley Diastase on Starch." Part I. By J. L. BAKER.

When the diastase from ungerminated barley is allowed to act at 50° on a solution of soluble starch, hydrolysis proceeds until at the end of an hour to an hour and a-half the constants of the dissolved matter are $[\alpha]_{D_{593}} = 160-165^\circ$ and $R_{593} = 60-65^\circ$. After this the reaction is a comparatively slow one, and if continued for ninety-six hours the reducing power is only increased to $R_{593} = 70$, the iodine reaction being still blue.

An examination of the products, after the reaction had proceeded for one and a-half to two hours, showed that a dextrin and maltose were the sole products. After twenty-four hours, evidence of the presence of glucose was obtained, the amount of this sugar apparently increasing in proportion to the time of conversion.

The dextrin, isolated by precipitation with alcohol from the products of the conversion, gave a blue iodine reaction, a specific rotation of $[\alpha]_{D_{593}} = 190-195^\circ$, and a reducing power of $R_{593} = 0.55-1^\circ$. The alcoholic solutions from which the dextrin was precipitated were collected and examined, and found to contain maltose, glucose if the conversion period was prolonged, but no trace of any dextrin of less complexity than described above.

Barley diastase acts on the above-mentioned dextrin very slowly, the constants of the solution after ninety hours at $45-50^\circ$ being $[\alpha]_{D_{593}} = 160^\circ$ and $R_{593} = 32^\circ$. The products, which give a blue iodine reaction, consist of maltose, unaltered dextrin, and glucose. The presence of glucose could be detected in eighteen hours, but after ninety hours the amount formed had only slightly increased. The action of malt diastase on this dextrin was more vigorous. After eighteen hours at 55° the solution, which no longer gave an iodine reaction, had the constants $[\alpha]_{D_{593}} = 149.3^\circ$ and $R_{593} = 50-51^\circ$. An examination of

the products showed that they consisted of maltose, a mixture of achroo-dextrins, and a considerable quantity of glucose.

Since barley diastase is without action on maltose, the glucose found in the products from the prolonged action of barley diastase on soluble starch must be derived from the dextrin. Barley diastase completely liquefies starch paste in two to three hours at 50°, the products consisting of the above described dextrin and maltose.

The dextrin obtained by the action of barley diastase on soluble starch or starch paste differs markedly from Nageli's "amylodextrin," which was re-investigated by Brown and Morris (*Trans.*, 1889, lv., 449). In consideration of its general behaviour and close relation to the parent substance starch, the author proposes to term the new dextrin α -amylodextrin.

DISCUSSION.

Mr. A. R. LING asked if the author had continued the reaction between barley diastase and soluble starch solution for a longer period than 144 hours, in fact until (when working with an excess of the diastase) the final point was reached. It had recently been shown by Mr. B. F. Davis and himself that by the action of the diastase from air-dried malt on starch paste below 60°, the whole of the starch was converted into maltose in forty hours. He had been struck by Mr. Baker's observation that maltose was practically the sole cupric-reducing compound formed in the early stages of the reaction between barley diastase and starch solution. With regard to the dextrin which the author had named α -amylodextrin, and which gave a blue iodine reaction, he could not help thinking, in view of what was known of starch-conversion products, that this dextrin (despite its apparent stability towards barley diastase) must have contained soluble starch. An indication of this was afforded by the behaviour of the dextrin towards malt diastase when the iodine reaction vanished.

Mr. BAKER, in reply, said that with regard to the suggestion of Mr. Ling and Dr. Thorne, that α -amylodextrin was a mixture of another dextrin and unaltered soluble starch, he was convinced that α -amylodextrin was an entity, from the fact that when this dextrin was acted on by barley diastase for eighteen hours at 50°, it split up into maltose and unaltered α -amylodextrin. If this residual α -amylodextrin was then subjected to the action of barley diastase under similar conditions, the same products were formed. This treatment had been repeated many times, and it did not seem possible that under such circumstances, soluble starch could escape the action of barley diastase.

*92. "The Decomposition of Chlorates. Part V. Potassium Chlorate in presence of Oxides of Manganese, and the Theory of Perchlorate Formation." By W. H. SODEAU, B.Sc.

In continuation of the previous work of the author, it was now shown that the amount of chlorine accompanying the oxygen evolved from potassium chlorate in presence of oxides of manganese was not increased on reducing the pressure under which the decomposition took place, whilst secondary reactions removing free chlorine from gaseous products have previously (*Trans.*, 1901, lxxix., 251) been experimentally shown to be greatly decreased on decomposition under reduced pressure. It was thus seen that no such secondary reaction occurred in the present case.

This excludes all theories which assume the cycle of changes to include the formation of a compound containing manganese and chlorine, or potassium and manganese, such as McLeod's well known theory. Oxygen being the only remaining constituent, it followed from this process of exclusion that the cycle of changes brought about by addition of oxides of manganese was confined to alternate oxidation and deoxidation (like the decomposition of hydrogen peroxide in presence of the same substances). It is probable that the formation of potassium perchlorate during the decomposition of the

pure chlorate by heat was due to an exothermic reaction independent of that which yielded chloride and oxygen. The non-production of perchlorate seemed to be the natural result of the addition of a substance (manganese dioxide) which brings about the transformation into chloride and oxygen at a temperature far below that at which the chlorate begins to give chloride and perchlorate.

DISCUSSION.

Prof. E. J. MILLS said that, in association with Mr. Stevenson, he had, some years ago, investigated the action of manganic oxide on potassic chlorate. They had not been able to find or prepare an oxide free from constitutional water, and any attempt to render the oxide anhydrous resulted in a loss of oxygen. Eventually, they used the oxide of Beilstein and Javorsky. Their work had reference chiefly to the question of catalysis, and they found that small quantities acted in proportion more energetically than large ones. It should be borne in mind that the composition of hot manganic oxide was affected by pressure. Altogether, it was a question whether the numerous difficulties besetting the investigation could be satisfactorily surmounted.

Mr. SODEAU, in reply, stated that in his examinations of the aqueous extracts of the residues, phenolphthalein was employed with precautions against carbon dioxide, and a very small fraction of the amount of alkalinity found by Prof. McLeod would therefore have been detected. The extracts were actually slightly acid, and the residual manganese peroxide rapidly absorbed potash from solution.

*93. "Studies in the Tetrahydronaphthalene Series. I. The Diazoamino-compounds of ar-Tetrahydro- β -naphthalene." By C. SMITH, B.Sc.

It has been shown by Bamberger and Bordt (*Ber.*, 1889, xxii., 625) that ar-tetrahydro- α -naphthylamine combines with diazonium salts, yielding azo-compounds.

The experiments of the author prove that ar-tetrahydro- β -naphthylamine behaves like a benzenoid amine, and yields diazoamino-compounds.

The following compounds have been prepared and examined:—

p - Toluenediazoaminotetrahydro - β - naphthalene, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{11}$, yellow crystals, m. p. 107°; readily soluble in alcohol and benzene, sparingly in petroleum. o - Nitrobenzenediazoaminotetrahydro - β - naphthalene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{11}$, orange-yellow crystals, m. p. 134°. p-Nitrobenzenediazoaminotetrahydro- β -naphthalene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{11}$, well-defined chocolate-brown crystals, melting at 179° with violent decomposition. p-Bromobenzenediazoaminotetrahydro- β -naphthalene, $\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{11}$, crystallises in lemon-yellow needles which decompose slightly on exposure to the air and melt at 134°. Diazoaminotetrahydro- β -naphthalene, $\text{C}_{10}\text{H}_{11}\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{11}$, well-defined, amber coloured crystals, m. p. 104°. β -Naphthalenediazoaminotetrahydro- β -naphthalene, $\text{C}_{10}\text{H}_7\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{11}$, crystallises in light yellow, lustrous plates, m. p. 137.5°. Tetrahydro- β -naphthaleneazo-8-naphthylamine, $\text{C}_{10}\text{H}_{11}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$, dark-red lustrous crystals moderately soluble in hot alcohol, m. p. 136°. Tetrahydro- β -naphthaleneazo- β -naphthol, $\text{C}_{10}\text{H}_{11}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, vermilion-red crystals with a green shimmer, m. p. 153°; it is insoluble in sodium hydroxide, and only sparingly soluble in hot alcohol.

DISCUSSION.

Dr. MORGAN pointed out that the mixed diazoamines of the tetrahydronaphthalene series are members of an extensive series of diazoamino-compounds having the general formula XN_3HY , which can be produced from one or other of the two pairs of generators, XN_2Cl , YNH_2 and YN_2Cl , XNH_2 , where X and Y are dissimilar aromatic nuclei derived from benzene, naphthalene (*Trans.*, 1902, lxxxi., 90), and tetrahydronaphthalene.

The genesis of these substances and their decomposition with mineral acids justify the belief that they are solid

solutions of the two compounds, XN_2NHY and YN_2NHX .

*94. "Experiments on Phosphorus Tetroxide." By C. A. WEST, B.Sc.

The author gave an account of the preparation of phosphorus tetroxide and of his attempts to determine its molecular weight. Methods based upon observation of the freezing- or boiling-points of a solution could not be used, no suitable solvent being found. At a red heat, under atmospheric pressure, the compound does not volatilise rapidly enough to allow of the determination of vapour density, but four concordant experiments at about 1400° led to the unexpected conclusion that the molecular formula is P_8O_{16} , that is twice what would have been expected from comparison with P_4O_6 and P_4O_{10} .

Some new determinations of the vapour density of phosphoric oxide at this temperature were also made. The mean of six concordant results gave 300.4 for the molecular weight P_4O_{10} requiring 284.

95. "The Decomposition of Compounds of Selenium and Tellurium by Moulds and its Influence on the Biological Test for Arsenic." By O. ROSENHEIM, Ph.D.

A paper has recently been published (Maassen, *Arch. f. Ges. A.*, 1902, xviii., 475) on the biological test for arsenic and the formation of organic compounds of arsenic, selenium, and tellurium by moulds. The author has been occupied for some time on the same subject in its connection with the detection of arsenic in beer and sugar, and had intended to publish his results in a more complete form. In view of Maassen's publication it has, however, been thought advisable to give a short *r  sum  * of the results in this direction confirming those of Maassen.

The biological test for arsenic (Gosio, *Ber.*, 1897, xxx., 1024) is said to be characteristic of this substance (Abel and Buttenberg, *Z. Hyg.*, 1899, xxxii., 449). The test consists in the formation of gaseous organic arsenic compounds, possessing a characteristic garlic odour, produced by the vigorous growth of certain moulds (*Aspergillus*, *Mucor*, and *Penicillium*) in media containing arsenic, and permits of its detection where chemical methods fail. When applying this test to certain substances (beer and sugar) which contained selenium and arsenic, the author noticed a pronounced faecal odour different from that produced by arsenic alone. It was thought that this was due to the presence of selenium, and experiments with soluble selenium compounds confirmed this view. It was also found that tellurium compounds were decomposed by *Penicillium brevicaulis*, giving rise to the production of a very characteristic odour. Owing to the extreme sensitiveness of the test with regard to arsenic, it was thought necessary to employ absolutely pure compounds of selenium and tellurium. The odour produced by the decomposition of selenium compounds is of a very disagreeable character (somewhat like skatol or mercaptan), whilst the gases formed by tellurium compounds possess a pronounced garlic odour. The test is extremely sensitive; 0.01 m.grm. in 1 c.c. of liquid is easily demonstrated by a vigorous growth of the mould. Unlike arsenic, pure selenium and tellurium are not attacked by the mould. It was found best to perform the test by using the medium proposed by Abel and Buttenberg (*loc. cit.*), namely, sterilised bread-crumbs, to which the sterilised liquid in question is added after infection with the mould.

The author has drawn attention elsewhere (CHEMICAL NEWS, 1901, lxxxiii., 277) to the influence of selenium on certain chemical tests for arsenic, and it is evident from the above results that in applying the biological test for arsenic, it is also necessary to take the possible presence of selenium (and tellurium) into consideration.

96. "Constituents of Gambier and Acacia Catechus." By A. G. PERKIN and E. YOSHITAKE.

The short paper on catechin, just published (Kostanecki and Tambor, *Ber.*, 1902, xxxv., 1867) renders it necessary to give the results of an investigation which has been in

progress for more than two years. The gambier catechu employed has been found to contain two catechins (b) and (c), and a third (a) has been isolated from the acacia catechu.

Catechin (b), $\text{C}_{15}\text{H}_{14}\text{O}_6$, air-dried, colourless needles, corresponds in its melting-point, $175-177^\circ$, with Gautier's (b) catechin (*Bull.*, 1879, xxx., 567), and gives, on fusion with alkali, phloroglucinol, protocatechuic acid, and an acid resembling acetic acid. The disazobenzene compound (compare Etti, *Monats.*, 1881, ii., 552), $\text{C}_{15}\text{H}_{12}\text{O}_6(\text{C}_6\text{H}_5\text{N}_2)_2$, salmon-red needles, m. p. $193-195^\circ$; its triacetyl derivative, $\text{C}_{15}\text{H}_9\text{O}_6(\text{C}_6\text{H}_5\text{N}_2)_2(\text{C}_2\text{H}_3\text{O})_3$, orange-red needles, m. p. $253-255^\circ$; pentabenzoyl catechin, $\text{C}_{15}\text{H}_7\text{O}_6(\text{C}_7\text{H}_5\text{O})_5$, colourless needles, m. p. $151-153^\circ$, and tetrabenzoyl catechin, prismatic needles, m. p. $171-172^\circ$, have been studied. Molecular weight determinations by the cryoscopic method of the two latter compounds confirm these formul  e.

Catechin (c), $\text{C}_{15}\text{H}_{14}\text{O}_6$, air-dried, contains no water of crystallisation, and forms colourless prisms, m. p. $235-237^\circ$. It yields an azobenzene compound, $\text{C}_{15}\text{H}_{12}\text{O}_6(\text{C}_6\text{H}_5\text{N}_2)_2$, orange-red needles, m. p. $215-217^\circ$, the acetyl derivative of which melts at $250-253^\circ$, and on fusion with alkali gives phloroglucinol and protocatechuic acid. It has been found at present only in minute quantity.

Catechin (a), $\text{C}_{15}\text{H}_{14}\text{O}_6$, H_2O (or less probably $\text{C}_{14}\text{H}_{14}\text{O}_6$, H_2O) air-dried, forms colourless needles, and corresponds in its melting-point, $204-205^\circ$ with Gautier's (a) catechin. Molecular weight determinations of the pentabenzoyl derivative (prismatic needles, m. p. $181-183^\circ$) coincide with this formula. The azobenzene compound, $\text{C}_{15}\text{H}_{12}\text{O}_6(\text{C}_6\text{H}_5\text{N}_2)_2$, needles, m. p. $198-200^\circ$, gives a triacetyl derivative, $\text{C}_{15}\text{H}_9\text{O}_6(\text{C}_6\text{H}_5\text{N}_2)_2(\text{C}_2\text{H}_3\text{O})_3$, orange-red leaflets, m. p. $227-229^\circ$. Fusion with alkali gave phloroglucinol, protocatechuic acid, and an acid resembling acetic acid.

Cyanomaclurin (*Trans.*, 1895, lxvii., 939), a constituent of *Artocarpus integrifolia*, has been found to contain a phloroglucinol group, and is probably isomeric with these catechins.

97. "The Decomposition of Oxalacetic Hydrazone in Aqueous and Acid Solution, and a new Method of Determining the Concentration of Hydrogen Ions in Solution." By H. O. JONES and O. W. RICHARDSON.

When oxalacetic hydrazone is heated with dilute acids it gives rise simultaneously to pyruvic hydrazone and carboxylic dioxide, and to pyrazolone carboxylic acid and water (Fenton and Jones, *Trans.*, 1901, lxxix., 92), the amounts of the former products being in the inverse order of the concentrations of the hydrogen ions in the solutions used. The hypothesis suggested to explain these observations was that the negative ion of the oxalacetic hydrazone underwent the first of the above decompositions when heated, whereas the undissociated molecule underwent the second.

Experiment shows that the results are better explained by supposing that the rate of decomposition into pyruvic hydrazone is proportional to the concentration of oxalacetic hydrazone, whereas the rate of formation of the pyrazolone carboxylic acid is jointly proportional to the concentration of the original substance and of the hydrogen ions.

The reaction was investigated in two ways, first the rate of evolution of carbon dioxide at a constant temperature (about 80°) was determined, and, secondly, the total amount of carbon dioxide given off at 100° was determined, in both cases water and sulphuric acid of different strengths being used. The results obtained agree with the requirements of the second hypothesis.

According to both theories, the amount of carbon dioxide produced satisfies the following equation,—

$$\log \left[\frac{1}{1 - \frac{C_2}{[C_2]_\infty}} \right] = \beta t,$$

where C_2 = concentration of pyruvic hydrazone (or amount

of carbon dioxide evolved) at any time t , $[C_2]_{\infty}$ its final concentration, and $\beta =$ a constant.

The hypothesis of the decomposition of the negative ion requires that β should decrease with increasing concentration of hydrogen ions, whereas the view here put forward requires that β should increase. Now it was found that β did increase with increasing concentration of hydrogen ions. This forms a crucial test between the two views.

A quick and easy method for determining the concentration of hydrogen ions in solution has also been worked out and tested.

Experiments have been made with the β -bromophenyl hydrazone of oxalacetic acid which decomposes in a similar way, and the results show satisfactory agreement with requirements of the theory stated above.

98. "The Dissociation Constants of Oxalacetic Acid and its Hydrazone." By H. O. JONES and O. W. RICHARDSON.

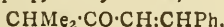
The authors have determined the dissociation constants of oxalacetic acid and its phenyl hydrazone. The conductivities of solutions of these substances were determined at 25°, and from the results the following values were obtained:—

For oxalacetic acid, $K = 1.33$. Oxalacetic hydrazone, $K = 0.11$.

99. "Derivatives of Butyrylpyruvic Acid." By A. LAPWORTH and A. C. O. HANN.

Certain points of interest arising out of the study of the Claisen reaction as applied to $\alpha\beta$ -unsaturated ketones (*Trans.*, 1901, lxxix., 1283) led the authors to study the action of ethyl oxalate and sodium on benzylideneisopropylmethylketone. The results were not those anticipated, but the following compounds have been prepared in the course of the work:—

Benzylideneisopropylmethylketone,—



is an oil (b.p. 274—276°). The oxime melts at 131—132° and the semicarbazone at 166—167°.

Ethyl isobutyrylpyruvate, $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, from isopropylmethylketone, ethyl oxalate, and sodium ethoxide, is a nearly colourless oil which boils and decomposes at 230—232°; it does not solidify at -15°. The copper, nickel, calcium, and other derivatives have been prepared. When the ester is hydrolysed with strong potassium hydroxide solution under certain conditions, and the resulting solution treated with excess of strong hydrochloric acid, a sparingly soluble compound is precipitated in quadratic plates. This is an acid potassium isobutyrylpyruvate having the composition $(\text{C}_7\text{H}_{10}\text{O}_4)_2 \cdot \text{C}_7\text{H}_9\text{O}_4\text{K}$; its solution gives a red coloration with ferric chloride, and becomes yellow on addition of excess of alkalis; it is only decomposed by a large excess of mineral acid; a similar sodium salt was not obtained.

Ethyl n-butyrylpyruvate, $\text{Pr} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, is similar in properties to the ester described above. When it is hydrolysed with potassium hydroxide, it yields a sparingly soluble acid potassium n-butyrylpyruvate crystallising in asbestos-like needles, which has, however, the composition $(\text{C}_7\text{H}_{10}\text{O}_4)_2 \cdot \text{C}_7\text{H}_9\text{O}_4\text{K}$. As in the former instance, this substance is very stable towards acids, and no corresponding sodium salt could be obtained.

100. "Sulphocampholenecarboxylic Acid." By A. W. HARVEY and A. LAPWORTH.

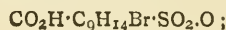
When the residues obtained by evaporating the last aqueous mother-liquors in the preparation of ammonium bromocamphorsulphonate were fractionally extracted with alcohol, a small quantity of a new substance dissolved and was obtained in the form of transparent, calcite-like crystals. A small quantity of this product has also been obtained by Dr. Kipping.

The compound has the formula $\text{C}_{10}\text{H}_{15}\text{SO}_3\text{NH}_4$, and it is the hydrogen ammonium salt of an unsaturated, monocyclic, sulphocarboxylic acid, $\text{CO}_2\text{H} \cdot \text{C}_9\text{H}_{14} \cdot \text{SO}_3\text{H}$, for which the name *sulphocampholenecarboxylic acid* is proposed. That it is unsaturated is shown by its aqueous

solution instantly decolorising bromine water and an ice-cold solution of potassium permanganate.

The normal barium and calcium salts, $\text{C}_{10}\text{H}_{15}\text{SO}_3\text{Ba}$ and $\text{C}_{10}\text{H}_{15}\text{SO}_3\text{Ca}$, crystallise well and are more soluble in cold than in hot water; the normal ammonium salt is very soluble in water. The hydrogen barium and hydrogen calcium salts crystallise in fine needles. The chloride and bromide do not crystallise readily.

When solutions of the salts are treated with bromine, a molecular proportion of the latter is at once absorbed, and a very sparingly soluble substance separates. This appears to be a sultonecarboxylic acid,—

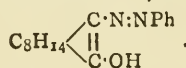


it crystallises from chloroform in small prisms, melts and decomposes at 155°, dissolves in alkalis and alkali carbonates, and is re-precipitated unchanged by acids.

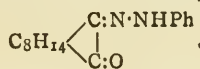
The investigation of the acid and its derivatives is in progress.

101. "Some Properties of Camphorquinonephenylhydrazone." By A. LAPWORTH and A. C. O. HANN.

It has been found by Betti (*Ber.*, 1899, xxxii., 1995) that camphorquinonephenylhydrazone ("camphormethylenehydrazone") usually exists as a mixture of two desmotropic forms. One of these melts at 180°, gives a reddish coloration with ferric chloride in benzene solution, and is therefore probably the enolic form,—



The other, melting at 155°, may be isolated by adding a trace of piperidine to a solution of the hydrazone in benzene; as it gave no distinct colour with ferric chloride, it was supposed to be the ketonic form,—



With Betti's permission, the authors have carefully studied the properties of the compound, and, although they are able to confirm all his statements with regard to the enolic form, they have not been able to isolate a second modification in the pure state, although there can be no doubt that one is present; they think that the substance melting at 155° must be a mixture of both forms.

The speed with which equilibrium between the two forms, in various media, is attained was investigated by observations of the mutarotation. Equilibrium appears to be reached most rapidly in alcoholic solution, a constant rotation being observed at once. In chloroform or benzene, however, the change occurs very slowly, as in 1 per cent solution at the ordinary temperature it occupies several days.

In benzene, with solutions varying in concentration from 0.1 to 1 per cent, the initial rotation, when the pure enol is used, is about $[\alpha]_D = +325^\circ$, and falls to between $+205^\circ$ and 290° according to the concentration. With all specimens of mixed material, even when prepared by Betti's method, a fall was invariably observed in dilute solution, indicating that the enol was still present in considerable amount.

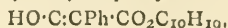
The effect of catalytic agents on the rate of change in benzene was carefully studied. Traces of bases, if not too weak, whether primary, secondary, or tertiary, accelerate the change, and, amongst others, ammonia, aniline, piperidine, pyridine, brucine, and strychnine were tried and found to be effective. Acids, on the other hand, retard the change, and it is possible to arrest the fall in rotation at any point desired by the addition of a minute quantity of trichloroacetic acid, when it will again proceed on addition of a trace of a base.

† In all cases, as was to be expected, the state of equilibrium was found to be independent of the catalytic agent

102. "Optically Active Esters of β -Ketonic and β -Aldehydic Acids. Part I. Menthyl Hydroxymethylene-phenylacetate." By A. LAPWORTH and A. C. O. HANN.

The authors propose to investigate certain aspects of the question of tautomerism involving the migration of hydrogen atoms by the employment of esters of β -ketonic and β -aldehydic acids with optically active alcohols of high molecular weight. It is hoped that the compounds may thus be obtained in a crystalline, and therefore more easily purified form, and that by observation of the change of rotation, further evidence with regard to certain obscure points may be obtained.

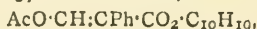
Menthyl hydroxymethylene-phenylacetate,—



may be prepared by the action of sodium on a mixture of menthyl phenylacetate and formate dissolved in anhydrous ether. It is precipitated from the aqueous solution of its sodium derivative on addition of acids as an oil which rapidly solidifies, and crystallises from light petroleum in transparent prisms or pyramids, which belong to the tetragonal system. These melt at $82-83^\circ$, and exhibit triboluminescence, which is sufficiently brilliant to be observed in broad daylight. Its freshly prepared 2 per cent solution in chloroform has $[\alpha]_D = -74.6^\circ$; this falls in a few days to about -71° . In absolute alcohol, the rotation is $[\alpha]_D = -64.9^\circ$, and falls only slightly, if at all, in course of time. Although its alcoholic solution is rapidly coloured violet by ferric chloride, its solution in ether or benzene is not affected unless it is boiled with the salt for some time, or a trace of a base is added, when a similar coloration develops. The solid probably represents the aldehydic form of the ester (Wislicenus, *Ann.*, 1900, cccxii., 34).

The copper derivative crystallises in green prisms which melt and decompose at $92-95^\circ$; the sodium derivative forms thin, transparent plates.

The phenylcarbamate, $\text{NHPh}\cdot\text{CO}_2\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, crystallises in long, slender needles melting and decomposing at $235-237^\circ$. The acetate,—



separates from ethyl acetate in needles melting at $51-52^\circ$.

The oxime is immediately precipitated as an oil on mixing solutions of the ester with one of free hydroxylamine or hydroxylamine acetate. With phenylhydrazine, the ester is converted into the diphenylpyrazolone which is obtained from the corresponding ethyl ester.

The enolic modification of the ester appears to be very unstable, and under conditions in which the liquid enolic ethyl ester may be obtained, the above compound was always produced. No evidence of the existence of isomeric copper or acetyl derivatives could be obtained.

(To be continued).

NOTICES OF BOOKS.

The New Volumes of the Encyclopædia Britannica. The Second of the New Volumes, being Vol. XXVI. of the Complete Work. London: *The Times*. Edinburgh: Adam and Charles Black. 1902. Pp. 763.

THIS, the second of the new volumes, includes all subjects whose titles come between A U S (Austria-Hungary) and C H I (Chicacole, a town of British India). In general appearance and contents this volume is quite up to the standard of excellence set by the first volume.

It includes, of course, many subjects which do not come within the range of the *CHEMICAL NEWS*; but, among the chemical and physical articles which appear, we must call special attention to the long and excellent essay on Bacteriology by Prof. H. Marshall Ward, D.Sc., F.R.S., who treats the subject in a general way; and the accompanying one by Dr. Robert Muir, who deals with the

pathological side of the question. Both these authors are known experts on the subject, and their names alone are sufficient guarantee of the value of the article. There are also two articles by Prof. H. L. Callendar, F.R.S., on Calibration and Calorimetry, both of which will well repay perusal; one on Cement, by Bertram Blount; and, most important of all, an article entitled "Chemistry," by Prof. H. E. Armstrong, F.R.S. This article fills about 40 pages of the *Encyclopædia*, and, long as it is, it is manifestly impossible to give more than a brief outline of this subject—the foundation of all the sciences—within such limits. However, Prof. Armstrong has treated the matter in a masterly manner, and has touched on practically every branch of the subject.

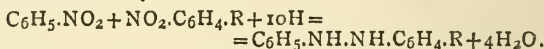
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 23, June 9, 1902.

A New Isomerism of Asymmetric Nitrogen.—E. Wedekind.—The presence of two atoms of asymmetric nitrogen in a molecule appears to render possible the existence of the stereo-isomeric salts which take part in various reactions. The author endeavours actually to find new examples of such isomerism, and he proposes to apply Pope's method to the stable form which can be split up into two active isomers.

Benzene-azobenzoic Aldehyde.—P. Freundler.—The author showed in a preceding research that it is not possible to apply Friedel and Crafts' reaction to azobenzene or to its derivatives, or to prepare by this method compounds of the type $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{R}$. On the contrary, however, the synthesis of such compounds can be easily effected by applying to a mixture of nitrated derivatives the general method of preparation of the hydrazoic and azoic compounds:—



By this means benzene-azo-*p*-benzoic aldehyde can be obtained, $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$. The author describes the formation of this compound and its principal properties. He now proposes to complete the investigation of the aldehydes, and to utilise the same reaction to prepare azoic derivatives with alcoholic and acid ketonic function.

MEETINGS FOR THE WEEK.

THURSDAY, 10th.—Institution of Mining and Metallurgy, 5. "The Diehl Process," by Hans C. Knutsen. "The Pierreite Concentrating Mill," by Mervyn S. Stutchbury.

ST. PAUL'S SCHOOL, West Kensington.—

An EXAMINATION will be held at the above School on Tuesday, September 16th, 1902, and the following days, for filling up Twenty or more Vacancies on the Foundation.—Full particulars can be obtained on application to the Bursar.

IMPERIAL COLLEGE OF CHEMISTRY,

49 & 51, IMPERIAL BUILDINGS, LUDGATE CIRCUS, E.C.

Principal—FREDERICK DAVIS.

An especial Course of Instruction has been organised for Fellows and Associates of the Institute of Chemistry, to meet the requirements of the Local Government Board, in Therapeutics, Pharmacology, and Microscopy, as recommended by the Council of the Institute.

THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2224.

THE MELTING-POINT OF CHROMIUM.

By ERNEST A. LEWIS.

As the melting-point of chromium has not been determined accurately I obtained some chromium of 99 per cent purity, and free from carbon made by the Goldschmidt process by reduction of chromium oxide with powdered aluminium, and determined the melting-point with a Le Chatelier pyrometer.

I took a piece of chromium as big as a pea and put it in a hole in a lump of quicklime, and then directed the flame of a blowpipe fed with coal-gas and oxygen on to it; when the chromium was melted the thermo-junction of platinum and platinum-iridium was placed in it, and the point at which the spot of light of the galvanometer was stationary a few seconds was noted. This is very difficult, as the junction is very often broken by being put into the molten chromium at a high temperature.

Two experiments gave the melting-point of chromium to be:—

No. 1	1510° Centigrade
No. 2	1520° "
Mean	1515° "

In standardising the pyrometer the following points were used:—

Boiling-point of water	100° C.
Melting-point of zinc	419° C.
Melting-point of aluminium	657° C.
Melting-point of copper (in air)	1065° C.

310, Dudley Road, Birmingham.

SANDALINA OIL AS A PRODUCT OF THE DECOMPOSITION OF GLUCOSIDES.

By Dr. T. L. PHIPSON.

THE name of sandalina has been given to a kind of petroleum which issues with the water from a spring at Santa Clara, in the island of Cuba. On account of the peculiar odour of the water it has been called the Sandalwood Spring. I have written to my friend Mr. Charles Thornton, C.E., to send me a sample of this water the first time he visits that neighbourhood; in the meantime, however, it has been examined by Mr. H. N. Stokes, who finds that the oil obtained is quite transparent and of the colour of amber. It has a specific gravity of 0.901, and a peculiar odour resembling that of cedar wood, and distills between 230° and 330° C. It appears, according to this chemist, to consist chiefly of naphthalenes. Naphthalene or petroleum acids, he says, are formed in notable quantity even in a rapidly conducted oxidation with chromic acid. The final products of oxidation are carbonic acid, acetic acid, and water (with traces of acetone and higher homologues).

Many years ago in examining certain glucosides discovered by me in the fruit of the walnut and the root of the strawberry (*Comptes Rendus* and *CHEMICAL NEWS*, 1869, and 1878), I observed the presence of a small quantity of an oily substance floating upon the liquid during the decomposition of these glucosides (regianine and fragarine) by boiling with dilute hydrochloric acid, and the odour of cedar wood was so strong that it diffused itself throughout the laboratory. Other glucosides, notably a remarkable one which I extracted some time ago from the *Ampelopsis*

(*Cissus quinquefolia*) gave a similar result, and I have little doubt that this odoriferous substance is the body now called sandalina; and just as Pasteur once told me that succinic acid is a constant product of the fermentation of sugar, it is probable that sandalina oil will be found a constant product of the decomposition of glucosides in the manner alluded to. I hope to refer again to this when I shall have been able to look over my former experiments with regianine and fragarine.

TWENTIETH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature, appointed by your body in 1882, respectfully presents to the Chemical Section its Twentieth Annual Report, covering the ten months ending June 1, 1902.

Works Published.

"A Bibliography of the Analytical Chemistry of Manganese, 1785—1900." By Henry P. Talbot and John W. Brown. City of Washington, published by the Smithsonian Institution, 1902. 8vo. viii. + 124 pp.

Smithsonian Miscellaneous Collections, Vol. XLI. (No. 1313).

"Index to the Literature of the Spectroscope" (1887—1900, both dates inclusive), [continuation of the previous index by the same author published in 1888]. By Alfred Tuckerman. Washington City, published by the Smithsonian Institution, 1902. 8vo. iii. + 373 pp.

Smithsonian Miscellaneous Collections, Vol. XLI. (No. 1312).

"Chemical Societies of the Nineteenth Century." By Henry Carrington Bolton. City of Washington, published by the Smithsonian Institution, 1902. 8vo. 15 pp.

Smithsonian Miscellaneous Collections, Vol. XLI. (No. 1314).

This contains a list of the serials published by the Societies, fifty-six in number, statistics of membership for 1900, &c.

"On a System of Indexing Chemical Literature," adopted by the Classification Division of the U.S. Patent Office. By Edwin A. Hill. *J. Am. Chem. Soc.*, xxii., No. 8; also *CHEM. NEWS*, vol. lxxxiv., 202 et seq. Oct.—Nov., 1901.

"A Bibliography of Photography," by Miss Adelaide M. Chase, was begun in the February number of the *Photo Era*, published at Boston. It is confined to literature in English, and does not include articles in photographic and chemical journals.

Notes of Foreign Bibliographies.

Krupsky, A. K. "Russkaya chast Khimicheskoy Bibliographii." S. Petersburg. 1900. 62 pp., 4to.

This is a reprint by the Imperial Academy of Sciences, St. Petersburg, of the Russian titles in Bolton's "Select Bibliography of Chemistry" (Vols. i.—iii.).

W. R. Whitney and J. E. Ober. "Index to the Literature of Colloids." *J. Am. Chem. Soc.*, vol. xxiii., p. 842. (Nov., 1901).

Glinzer, Langfurth, und Voigtländer. "Sammelkatalog der in Hamburger öffentlichen Bibliotheken vorhandenen Litteratur aus der Chemie und aus verwandten Wissenschaften." Hamburg, 1901. 108 pp. 8vo.

* Advance proofs from *Proceedings of the American Association for the Advancement of Science*, 1902, vol. li.

Garçon, Jules. "Répertoire général ou Dictionnaire méthodique de bibliographie des industries tinctoriales et des industries annexes." Paris, 1900-1901. 3 vols., roy. 8vo. 1978 pages in the three volumes.

This completes the work noticed in the Eighteenth Annual Report.

Works in Progress.

The MS. of an "Index to the Literature of Thorium," by Cavalier H. Joüet, Ph.D., of Columbia University, New York, has been examined by each member of your committee, and recommended for publication to the Smithsonian Institution. It is now being prepared for printing.

Mr. Benton Dales, of Cornell University, has in preparation "An Index to the Literature of the Yttrium Group of the Rare Earths."

Reports of progress have been received from Messrs. Frank R. Fraprie and H. Carrington Bolton.

It is the sad duty of the committee to record the death of one of its original members, Professor Albert R. Leeds, Ph.D., long Professor of Chemistry in the Stevens Institute of Technology, Hoboken, N.J. His contributions to chemical bibliography include "Indexes to the Literature of Ozone," and of "Peroxide of Hydrogen."

It is gratifying to note the increasing and continued interest in bibliography on all sides, and the committee stands ready to encourage the movement in chemistry by practical assistance to those desirous of contributing to the now considerable list of indexes. Address correspondence to the Chairman, at the Cosmos Club, Washington, D.C.

Committee:—

H. CARRINGTON BOLTON (in Europe),
F. W. CLARKE,
A. B. PRESCOTT,
ALFRED TUCKERMAN,
H. W. WILEY.

APPENDIX.

Bibliographies Named in Reports, I-XX., 1883-1902.

The following list includes only those bibliographies that have been published under the auspices of the committee, or independently, as monographs and separates.

Copies may be obtained, so far as available, on application to the Society or Institution issuing them, or in some cases by addressing the authors.

Aceto-Acetic Ester, Bibliography of. By Paul H. Seymour. Smithsonian Miscellaneous Collections, No. 970. Washington, 1894. 8vo.

Carbides, Review and Bibliography of the Metallic. By J. A. Mathews. Smithsonian Miscellaneous Collections, No. 1090. City of Washington, 1898. Pp. 32, 8vo.

Cerium and Lanthanum, Indexes to the Literature of. By W. H. Magee. Smithsonian Miscellaneous Collections, No. 971. Washington, 1895. Pp. 43, 8vo.

Chemistry, A Select Bibliography of; 1492-1892. By Henry Carrington Bolton. Smithsonian Miscellaneous Collections, Nos. 850. Washington, 1893. Pp. 1212, 8vo.

First Supplement, S. M. C., No. 1170, 1899.

Section VIII., Academic Dissertations, S. M. C., No. 1253, 1901.

Columbium, Index to the Literature of; 1801-1887. By Frank W. Traphagen. Smithsonian Miscellaneous Collections, No. 663. Washington, 1888. Pp. iv.+27, 8vo.

Didymium, Index to the Literature of; 1842-1893. By A. C. Langmuir. Smithsonian Miscellaneous Collections, No. 972. Washington, 1895. Pp. 20, 8vo.

Explosives, Index to the Literature of; Part I. By Charles E. Munroe, Baltimore, 1886. Pp. 42, 8vo. Part II., Baltimore, 1893. Pp. 43-195, 8vo.

Electrolysis, Index to the Literature of; 1784-1880. By

W. Walter Webb. Annals of New York Academy of Sciences, vol. ii., No. 10, 1882. Pp. 44, 8vo.

N.B.—This has been translated into French by Donato Tommasi, Paris, 1889.

Heat, Dictionary of the Action of Heat upon certain Metallic Salts, including an Index to the principal literature upon the subject. Compiled and arranged by J. W. Baird; contributed by A. B. Prescott, New York, 1884. Pp. 70, 8vo.

Light, Chemical Influence of, A Bibliography of. Alfred Tuckerman. Smithsonian Miscellaneous Collections. No. 785. Washington, 1891. Pp. 22, 8vo.

Manganese, Index to the Literature of; 1596-1874. By H. Carrington Bolton, Annals of the Lyceum of Natural History, New York. Vol. xi., November, 1875. Pp. 44, 8vo.

Manganese, Analytical Chemistry of; A Bibliography of the. By Henry P. Talbot and John W. Brown. Smithsonian Miscellaneous Collections, No. 1313. City of Washington, 1902. Pp. 8vo.

Morphine, Chemical Bibliography of; 1875-1897. By H. Brown. Pharmaceutical Archives. Vol. i., No. 3. No date, no place. Pp. 60, 8vo.

Ozone, Index to the Literature of; 1785-1879. By Albert R. Leeds, Annals of the New York Academy of Sciences. Vol. i., No. 12, 1880. Pp. 32, 8vo.

Ozone, Index to the Literature of; 1879-1883. Accompanied by an Historical, Critical Résumé of the Progress of Discovery since 1879. By Albert R. Leeds. Annals N. Y. Academy of Sciences. Vol. iii., p. 137. 1884. Pp. 16, 8vo.

Peroxide of Hydrogen, Index to the Literature of; 1818-1878. By Albert R. Leeds. Annals of the New York Academy of Sciences. Vol. i., No. 13, 1880. Pp. 11, 8vo.

Peroxide of Hydrogen, Index to the Literature of; 1879-1883. By Albert R. Leeds. Annals of New York Academy of Sciences. Vol. iii., p. 153, 1884. Pp. 3, 8vo.

Platinum Group, A Bibliography of the Metals of the. Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium, 1748-1896. By James Lewis Howe. Smithsonian Miscellaneous Collections, No. 1084. City of Washington, 1897. Pp. 318, 8vo.

Spectroscope, Index to the Literature of. By Alfred Tuckermann. Smithsonian Miscellaneous Collections. No. 658. Washington, 1888. Pp. x.+423, 8vo.

The same, 1887-1900, both dates inclusive. S. M. C., No. 1312. Washington City, 1902. Pp. iii.+373, 8vo.

Starch Sugar, Bibliography of. By Edw. J. Hallock. Appendix E to Report on Glucose prepared by the National Academy of Sciences, in response to a request made by the Commissioner of Internal Revenue. U.S. Internal Revenue, Washington, D.C., 1884. Pp. 44, 8vo.

Tannins, Index to the Literature of. By Henry Trimble. The Tannins. Philadelphia, 1892. Vol. i., Appendix. Vol. ii., Philadelphia, 1894.

Thallium, Index to the Literature of. By Martha Doan. Smithsonian Miscellaneous Collections, vol. xli., No. 1171. Washington, 1899. Pp. 26.

Thermodynamics, Index to the Literature of. By Alfred Tuckerman. Smithsonian Miscellaneous Collections. No. 741. Washington, 1890. Pp. vi.+329, 8vo.

Thorium, Index to the Literature of. By Cavalier H. Joüet. Smithsonian Miscellaneous Collections, No. —. [In press].

Titanium, Index to the Literature of; 1783-1876. By Edw. J. Hallock. Annals of the New York Academy of Sciences. Vol. i., Nos. 2 and 3, 1877. Pp. 22, 8vo.

Uranium, an Index to the Literature of; 1789-1885. By H. Carrington Bolton. Smithsonian Report for 1885. Washington, 1885. Pp. 36, 8vo.

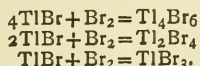
Vanadium, Index to the Literature of. By G. Jewett Rockwell. Annals of the New York Academy of Sciences, vol. i., No. 5, 1877. Pp. 32, 8vo.

Zirconium, Index to the Literature of. By A. C. Langmuir and Charles Baskerville. Smithsonian Miscellaneous Collections, No. 1173. City of Washington, 1899. 29 pp. 8vo.

THE ACTION OF BROMINE ON THALLOUS CHLORIDE IN THE PRESENCE OF WATER. COMPOUNDS OF THE TYPE Tl_2X_4 .

By V. THOMAS.

I. The per-salts of thallium, such as the tribromide, $TlBr_3$, when treated with appropriate quantities of thallous bromide, give rise to intermediate salts, Tl_2Br_4 and Tl_4Br_6 . The problem of the formation of these intermediate salts appears as if it ought to be solved in a much more simple manner by the successive addition of bromine to thallous bromide. The experiment is easy to carry out, and the results seem *à priori* to leave no doubt as to the regular fixation of the bromine on the proto-salt. It is only necessary to take a few elementary precautions to obtain, according as we wish, either Tl_4Br_6 or Tl_2Br_4 . The reactions are then easy to express:—



This regular fixation of bromine on the thallous chloride is, however, only apparent. In fact, it results from very complex reactions which are effected in the body of the solution.

The bromisation of thallous bromide does not lend itself very well to the study of these reactions. These reactions are, on the other hand, very distinctly observed in the fixation of bromine on the chloride $TlCl$. By admitting the fact of the regular fixation of the halogen we ought to obtain as product of the reaction Tl_4Cl_2Br and $Tl_2Cl_2Br_2$. Experience shows that we generally obtain bodies altogether different; in particular, the addition of one atom of bromine to two molecules of the chloride leads to the chlorobromide, $Tl_4Cl_3Br_3$. Everything seems to pass as if, in the cold, there was a displacement of a part of the chlorine by the bromine and a simultaneous fixation of the bromine on the product formed.*

Now, under the conditions of the experiments the displacement of the chlorine by the bromine appears to be so singular as to be inadmissible. We think that all the facts we shall state later on agree very well with one of the following hypotheses:—

1. The addition of a quantity of bromine, however small it may be, to thallous chloride gives rise to a thallic chlorobromide of the normal addition $TlClBr$.†

This latter, in the presence of an excess of thallous chloride, is reduced with the formation of chlorobromides belonging to the types Tl_4X_6 and Tl_2X_4 . The reduction to the state of intermediate chlorobromides is never complete. All these chlorobromides are, in fact, dissociated on contact with water, and can only exist in the presence of a variable quantity of the thallic salt.

2. The bromine becomes fixed regularly on the thallous chloride, giving normal derivatives of addition, such as $Tl_4Cl_2Br_2$ and $Tl_2Cl_2Br_2$, but these being dissociable on contact with water, decompose immediately into per-salts and less chlorobromised salts.

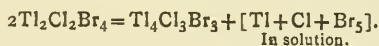
II. If to a small quantity of thallous chloride suspended in water we add an excess of bromine the thallous chloride is rapidly dissolved with an accompanying rise of tem-

perature. The solution obtained by evaporation in the air rapidly takes a syrupy consistence, and at the same time it deposits a small quantity of black oxide, Tl_2O_3 , the product of a secondary reaction, the hydrolysis of the chlorobromide formed. At this moment the solution contains a hydrated thallic chlorobromide, $TlClBr_2$, which is very unstable. If we continue the evaporation *in vacuo* over sulphuric acid we obtain a product of decomposition of this chlorobromide of the type Tl_2X_4 with the composition $Tl_3Cl_2Br_4$. Finally, this latter in the presence of water decomposes in the same way as the bromide of thallium, giving rise to a thallic compound, which dissolves, and to a compound of the type Tl_2X_3 , which is precipitated on account of its slight solubility.

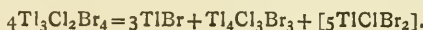
By proceeding in the inverse manner, that is to say, by adding to equal quantities of thallous chloride increasing quantities of bromine, we pass from the compounds of the type TlX to the compounds Tl_2X_3 , Tl_2X_4 , and Tl_2X_6 .

III. By adding an excess of bromine to thallous chloride and evaporating the solution thus obtained *in vacuo*, we can easily obtain the chlorobromide $Tl_3Cl_2Br_4$. (For the details of this preparation see *Bull. Soc. Scient. et Méd. de l'Ouest.*, vol. x., p. 11). It occurs in small transparent prisms, apparently orthorhombic, of a sulphur-yellow colour, and which appear to become tarnished after prolonged exposure to the air.

On contact with water it decomposes according to the equation:—



In every case we obtain, at the same time as the chlorobromide $Tl_4Cl_3Br_3$, a small quantity of thallous bromide; this latter apparently being formed by a decomposition which can be represented by the equation (*Bull. Soc. Scient. et Méd. de l'Ouest.*, vol. x., p. 12—14):—



The hydrochloric acid in solution reacts on the $Tl_3Cl_2Br_4$ in the same way as water; in any case the chlorobromide formed, Tl_2X_3 , is again submitted to the action of the acid, and appears to be brought back to the type TlX . Hydrobromic acid behaves in a similar manner, but the reaction is a little more complicated, the hydrochloric acid being displaced by the hydrobromic acid, at least to some extent.

The oxygenated acids, sulphuric acid, and nitric acid, for example, set a large quantity of the halogen at liberty, especially when heated.

Under the action of heat, at about 150° , the colour of this last salt becomes rather deeper, then at 165° it melts, giving a yellow liquid, and undergoing slight decomposition. At a higher temperature the decomposition is much more rapid, large quantities of bromine are given off, and if we have taken care not to heat too strongly, but only just up to 360° , the residue consists of an orange-coloured mass approaching red, formed of small flakes, very probably belonging to the type Tl_4X_6 .—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 11.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., The Duke of Northumberland, K.G., President, in the Chair. Mrs. Baily, Miss L. M. Burnett, the Rt. Hon. Sir Ernest Cassel, K.C.M.G., Lady Kelvin, Miss F. A. Musgrave, Mrs. E. Otter, and Mr. E. Schweich were elected members.

Sewage Disposal.—On the advice of Professor Henry Robinson, M.Inst.C.E., the District Council of Malling, Kent, have decided to lay down the latest type of bacteria beds for Aylesford and Burham, and have sealed a contract for the supply of Candy Automatic Revolving Sprinklers, and Patent Intermitters, for distributing the sewage over the surface of the beds.

* It must be well understood that we do not here advance any hypothesis as to the order in which these two operations might take place.

† This chlorobromide can be easily prepared, and will be described later on.

RECENT DEVELOPMENTS IN COLOURING-MATTERS.*

By Geheimrath Professor OTTO N. WITT, Ph.D. F.C.S.,
of Berlin.

THE love of colour is innate in the human mind, and this alone, if nothing else, would be sufficient to account for the interest with which the coal-tar colour industry has met from its beginning. In England especially its progress has been watched with great attention, and only two days ago the Vice-Patron of this Institution, His Royal Highness the Prince of Wales, has shown by some remarks, made in his Opening Address of the New Technical Institute at Bushey, that the interest taken in this subject has in no way abated.

Artificial colouring-matters have formed so often the subject of more or less popular lectures, and this subject has been treated with such ability by eminent scientists, that it becomes difficult to show this domain of chemistry in a light new and interesting to an audience such as I have to-day the honour to address. Many years ago you have seen in this room the early achievements of the newly-created industry, marvellous for their beauty and brilliancy. Later on the progress of this industry has been duly recorded. More recently still it has become the custom in this country to view colour-making not so much from its chemical or industrial side, as from the standpoint of the national economist, who contemplates the values produced by industrial enterprise, and investigates the reasons why these values should be unevenly distributed amongst the different nations, striving side by side for progress and engaged in friendly, yet none the less eager competition.

I may say at once, that I have no intention to treat my subject from either of these points of view. I take it for granted, that everybody is acquainted with the marvellous variety and brilliancy of artificial dye-stuffs, and I am too much of a chemist and too little of an economist to offer any original or valuable view about that side of the question which I have just mentioned. But I shall make an attempt to trace in this lecture the influence of the development of theoretical chemistry on the progress of the colour industry. If in so doing I should refer now and then to theoretical points without being able to explain them in detail, I hope to be forgiven.

In beginning this lecture allow me briefly to refer to the history of it.

When I received from Sir William Crookes the flattering invitation to speak before you this evening, my thoughts naturally wandered back to some recollections in connection with this Institution. I remembered vividly several brilliant lectures to which I had the privilege of listening in this room, where the spirits of Davy and Faraday, of Graham and Huxley, of Würtz and of my immortal friend A. W. von Hofmann seem still to be hovering. I felt loth to raise my own voice in such hallowed precincts. But then I also remembered an almost forgotten episode in my own life, which I ask your permission to tell.

I remembered, that almost exactly five-and-twenty years before receiving this invitation, I, then a very young chemist, had read before the Chemical Society of London a paper containing a then somewhat daring speculation on the connexion of the constitution of colouring-matters with their properties, a paper which the Publication Committee refused to print. A lively discussion followed, which was wound up by some encouraging remarks from the President, the late Mr. De la Rue. He said that he hoped that this speculative paper would prove useful in clearing up the complicated domain of colouring-matters, and that perhaps on some future occasion I should be in a position to place before the world, in a *Royal Institution lecture*, the results which had been obtained by its help.

This strange reminiscence, coupled with the curious

fact that Mr. De la Rue's prophetic words were fulfilled just when the period commonly assigned to a Jubilee had elapsed, gave me the courage to accept Sir William's kind invitation. For though I have done comparatively little towards the increase of our knowledge of colouring-matters, the five-and-twenty years past have sufficed to shed a brilliant light on what Mr. De la Rue could then justly call a very imperfectly known domain of chemistry, and innumerable facts brought to light during this period by a whole army of assiduous workers are now by common assent being classified under a theory which is neither more nor less than the suggestions contained in that rejected paper of mine, which I had fortunately published in another journal.

I may add, that I have been guilty in later times of another theory, which refers to the domain of dyeing, and which has still many opponents. This theory is the direct outcome of the theory of colouring-matters, and may be illustrated by some simple, yet striking experiments, some of which I intend to show you.

A fundamental question in the chemistry of dye-stuffs, and one not at all easy to answer, is this: "What is a dye-stuff?" Clearly it is something totally different from a substance only endowed with the power of selective absorption of light, a power which causes it to appear coloured. We know now that there are more substances in creation which possess this power than bodies which lack it. In this very room we have learned that the air itself, through which the solar rays penetrate on to the surface of the earth, is blue and not colourless, as we used to think. But even if we leave out of the question such faintly coloured substances as air and water, if we restrict our consideration to compounds endowed with a very intense power of selective absorption and at the same time soluble in the water which we employ for preparing our dye-baths, we do not arrive yet at the true definition of the dye-stuff. Cupric salts, soluble chromates, and many other intensely-coloured bodies are no dye-stuffs, as may be easily shown by experiment. Yet these compounds penetrate into the interior of textile fibres which are immersed in their solution. They must do so, according to the laws of Osmose so ably expounded by Thomas Graham, because they are crystalloids and the fibres are invariably colloids.

We know now that the laws of Osmose are identical with the laws governing solution, and that crystalloids are able to wander into the interior of colloids because they are soluble in their substance. Osmotic processes may be observed between two liquids which cannot be mixed with each other, just as well as between a liquid and a colloid immersed into it. Consequently we are justified in assuming that the same powers are at work in both cases.

In my first experiment (Exp. I.)* I intend to show you that a crystalloid, dissolved in some liquid such as water, and brought into contact with another liquid, not miscible with the first, such as ether, will either remain indifferent to the ether altogether, or it will leave the water and wander into the ether, or it will be distributed according to a certain ratio between the two solvents. In this latter case we have reason to believe that a constant interchange of molecules takes place between the two solutions. Clearly, this will only happen if there exists no great difference in the solubilities of the crystalloid in water and in ether. In that case the water will continually abstract nearly as many molecules of the crystalloid from the ether as the latter will take up from the water, and thus an equilibrium will be reached. If, on the other side, there is a great dissimilarity in the solubility of the crystalloid in the two solvents, then this process of mutual interchange will become so one-sided that it practically amounts to

* Details of experiment: An aqueous solution of magenta does not yield its colouring matter to ether; indophenol, on the contrary, is entirely taken up by ether. The dye-stuff, which is partly taken up by ether, is also a member of the indophenol group, the constitution of which is not yet fully established.

* A Lecture delivered at the Royal Institution of Great Britain, Friday, March 21, 1902.

the absorption of the whole of the crystalloid by one of the solvents.

My second experiment (Exp. II.)* is a more striking illustration of these fundamental facts. If we mix together two coloured solutions, one an aqueous one of a substance much more soluble in ether than in water, and the other an ethereal one of a substance more soluble in water than in ether, then the two solutions, on shaking, change colour, and their shades are reversed.

According to my theory, the process of dyeing, considered so problematical by many experts in this ancient and useful art, is strictly analogous with this wandering of molecules governed by the laws of solution, which we can so easily observe and control in operating with two non-miscible liquid solvents.

In my next experiment (Exp. III.)† we see that a dye-stuff wanders from the bath on to the fibre in much the same way as it wandered from water into ether. And if the fibre be previously dyed with a colouring matter little soluble in its substance, then this may be expelled and replaced by another of greater solubility. (Exp. IV.)‡

We see now that, in order to become a dye-stuff, a substance must not only be so intensely coloured that it can communicate its own shade to colourless substances holding it in solution; it must not only be soluble in water or any other liquid suitable for preparing a dye-bath; but it must also be soluble, and even much more soluble than in water, in the colloid, which forms the substance of the textile fibre. The finished dyed fabric is nothing more nor less than a solid solution of the dye-stuff in the substance of the fibre, unless there are secondary chemical influences, such as that of the mordants, at work, which change the solution into a suspension by precipitating the dye-stuff after its immigration into the fibre.

This peculiar combination of solubilities is very rarely met with amongst the coloured substances of an anorganic nature. In the vast domain of organic compounds of the aliphatic series we meet with very few dye-stuffs, because its members are mostly colourless, or but very faintly coloured. In the aromatic series, on the contrary, the power of selective absorption of light is so very frequent, that it would be very curious indeed if just that combination of solubilities, which is the making of the dye-stuff, were not of common occurrence. Taking as a basis the universally admitted axiom, that the physical properties of every compound are direct functions of its molecular constitution, we may easily believe that that peculiar combination of solubilities which I have shown to be the characteristic feature of the dye-stuff, would be the result of certain general conditions fulfilled in the constitution of many members of the aromatic group. My theory, proposed five-and-twenty years ago, was nothing else than an attempt to ascertain these general conditions by investigating the constitutional peculiarities of all those dye-stuffs the constitution of which had been fully established in those days.

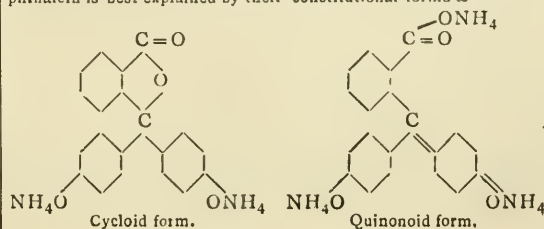
I have no intention to tax your patience by explaining in detail the results of that old investigation. It will be sufficient to summarise them by saying that in the molecule of every colouring matter, the constitution of which has been ascertained to this day (and there are many thousands of them), certain atomic constellations have been observed which seem to be essential, and of which always two must be present. One of these constellations is a group of atoms, which is the cause of the selective absorption of light. This group of atoms I call a *chromophore*. The number of atomic groups endowed with chromophoric properties amounts at present to about two dozen, and is being constantly increased by the progress of chemical research. All the chromophores, however, have that in common, that they are unable to exert their

influence unless they are helped by the presence of another group of atoms, which I call the *auxochromic* group. Very few auxochromic groups are known, and they belong to those which occur most frequently in the whole domain of organic chemistry—the amino group in its various forms, the hydroxyl group occurring in all the phenols, the sulpho- and the carboxyl group. None of these will cause a substance to become a dye-stuff unless this substance also contain a chromophore, but the latter is equally helpless if deprived of the assistance of the auxochromic group. Thus we meet in the molecular world that condition of the necessity of mutual help and assistance between two heterogeneous forms, which we can also trace in Sociology, a fact the establishment of which will no doubt be greeted with satisfaction by the ladies in this audience.

Our ideas on the nature and constitution of those groups which may act as chromophores have of course undergone many changes. Undoubtedly there must exist a law which governs the formation of chromophoric groups, but so far this law has not been definitely established. Some progress has, however, been made towards this end. At first the chromophores which we had gradually collected formed rather a motley crowd, and seemed to have no points in common. At present chemists working in this domain are inclined to attribute a quinoid structure to the great majority of colouring-matters. If this view be correct, then all these substances would be derivatives, not of benzene and its congeners, but of hydrocarbons containing two hydrogen atoms more in their molecule, derived from dihydrobenzene as a prototype. As sometimes it is almost impossible to decide in favour of one view or the other, the convenient hypothesis of tautomerism was resorted to, but in some cases we have been able to establish definitely the quinoid formula. Such is the case with the large and brilliantly-coloured group of dye-stuffs called phthaleins, which, according to modern view, must be considered as quinoid derivatives of benzoylbenzoic acid. The experiments which lead to this conclusion are so striking, that I cannot refrain from producing one of them, which has never been shown yet, though the time at my disposal does not allow its exhaustive discussion from a theoretical point of view. If we dissolve the well-known phenolphthalein in anhydrous ether containing some ammonia, the solution is perfectly colourless, but if we add ordinary water to this solution (Exp. V.), it assumes a beautiful red colouration. This peculiar fact that water alone is sufficient to cause the formation of this colour is perfectly incomprehensible if the old views on the constitution of phthaleins, which are still given in the majority of text-books, be adhered to, but it is exactly what we might expect to happen if we assume that the ammonium salt of phenolphthalein possesses a cycloid constitution in its ethereal solution, and that it is isomerised into the quinoid form by the addition of water.*

Thus our knowledge of the chemical causes of the physical properties of colouring matters is continuously developing. Quite lately we have even begun to form definite views about the connection of the chemical constitution of aromatic substances with that peculiar form of selective absorption of light which we call fluorescence,

* The isomerism of the two forms of the ammonium salt of phenolphthalein is best explained by their constitutional formulae—



* The ethereal solution used contained magenta acetate, whilst the aqueous one was prepared with trichloro-indophenol.

† In Exp. III. wool was dyed with erythrosine in the ordinary way, whilst in Exp. IV. a cotton cloth, previously dyed with patent blue, was treated in a bath of Congo red.

and which has formed, from the physical point of view, the subject of the masterly investigations of Sir Gabriel Stokes. The phenomenon of fluorescence is very frequently met with in dye-stuffs, and in the raw materials used for their manufacture. It can be exhibited in a very striking way with the help of electricity, either by allowing an arrow of electric light to penetrate into the solution of a fluorescent substance or by working a Geissler tube of suitable shape submerged in such a solution (Exp. VI.). The fact that the fluorescence of many substances is chiefly caused by the ultra-violet light, I shall try to demonstrate by the following somewhat delicate experiment: I have here, submerged in a solution of eosine, a Geissler tube, the lower part of which is ground out of a piece of rock-crystal, whilst the upper half is made of glass. When the electric current passes this tube the fluorescence round the quartz part of it is stronger than that in the neighbourhood of the glass, because the latter absorbs a good deal of ultra-violet light, whilst the quartz is almost free from such absorption. (Exp. VII.)

An immense amount of patient work has been accomplished by many chemists in the hope of establishing definite views on the constitution of the azo-colours, that group of dye-stuffs the introduction of which into the colour industry was the direct consequence of our early efforts to cast off empiricism, and to conduct our search for new colouring-matters according to definite scientific principles. Simple and transparent as the constitution of azo-colours appears to be if viewed superficially, yet it offers some problems of extraordinary difficulty, which have not been solved so far. But fortunately these difficulties have in no way interfered with the technical development of this family of dye-stuffs, which has been for a whole quarter of a century one continued and unparalleled series of successes. The process for producing these dye-stuffs is of the greatest simplicity. It consists in pouring together (Exp. VIII.) cold aqueous solutions or suspensions of diazo-compounds and phenols or amines. The dye-stuff is formed at once in a state of absolute purity, and with a yield absolutely theoretical; it need only be collected and dried to form a saleable product. No wonder, then, that these dye-stuffs gradually became the leading ones, and to a great extent superseded the old empirical products which were concocted in many complicated operations, with yields very far from satisfactory. As the number of diazo-compounds and of phenols and amines at our disposal is very large, the number of dye-stuffs which may thus be prepared is quite extraordinary; it has been computed, according to the rules of permutation, 3,159,000 different individual dye-stuffs have thus been proved to be at present easily accessible to our industry. Of these at least 25,000 form the subject of German patent specifications and of corresponding specifications in England, France, the United States, and other countries. Over five hundred are regularly manufactured on the larger scale.

The prolific nature of the azo-colour reaction explains the fact, that in this group we can choose, much better than in any other, substances possessing that ratio of solubilities in water and in the colloid substance of the various textile fibres, which we require. We can produce quite at will, azo-dye-stuffs which dye wool or silk or cotton, which dye slowly or quickly, which will stand soap or acid or alkali. This possibility of adjusting the chemical properties of dye-stuffs with an almost mechanical precision has been the cause of one of the greatest successes of the colour industry, the introduction of what is now known under the name of "substantive dye-stuffs," an expression which means dye stuffs that will dye cotton and other vegetable fibres from a simple aqueous dye-bath without the use of any mordant. The difference of the solvent power of cellulose and of water is for the vast majority of dye-stuffs so small, that the process of dyeing vegetable fibres with these ordinary colouring-matters can only be compared to that case of the joint action of ether and water on some substance soluble in both these solvents, where an almost equal division of

this substance takes place between the two solvents. Such cases exist as you saw in the first experiment. It is amongst the azo-dyes that we have found compounds which are so much more soluble in cellulose than in water, that they readily leave their aqueous solution and take up their abode in the fibre. And we have not only found these dye-stuffs but also the law which governs this most valuable abnormal solubility; it appears in all azo-colours which are prepared with diazo-compounds derived from symmetrical para-diamines. A novel and extremely fertile field for a systematic search for new dye-stuffs was thus opened, a field which has occupied hundreds of busy workers for many years, many of whom carried home a rich reward.

But whilst this field bore its rich harvest, others were by no means neglected. The search for dye-stuffs, which will dye cotton without a mordant, could not make us forget that just those colouring-matters which imperatively demand the use of mordants are those which from times immemorial have been used in preference for the production of fast and lasting shades. The brilliant synthesis of alizarine by Graebe and Liebermann, which made the world ring with admiration early in the seventies, had given us ample proof that the old, and to this day not wholly forgotten axiom, that there are two kinds of dyes—natural ones, which are fast, and artificial ones, which are fugitive—was a preconceived idea, totally devoid of any scientific foundation. The enormous financial success of the alizarine industry formed a tempting invitation to search for other dye-stuffs, which, similar to alizarine, would be endowed with the power of forming almost indestructible lakes with mordants of a sesquioxycid nature. Here too, like everywhere in science, we have marched for some time on the paths of empiricism, but here too logical deduction has come to our aid in disclosing the laws which govern the formation of lakes. In this case it is not (as in the substantive azo-dyes) the carbonic nucleus which determines the physical properties (viz., the ratio of solubilities) of the dye-stuff, but it is the peculiar position of the auxochromic groups contained in the molecule which governs its chemical properties. We know now that a dye-stuff must contain, in order to be able to form lakes with sesquioxycid mordants, two hydroxyl groups in juxtaposition. If this condition be fulfilled, the dye-stuff will dye in the same way and with equal fastness as alizarine, even if it be no derivative of anthracene, like the early alizarine dyes; and if these two hydroxyl groups or a suitable equivalent for them be missing, it will lack all power of dyeing mordants, even though derived from anthracene. With this law once established the synthesis of mordant dye-stuffs became a very easy matter, and to-day there is hardly a group of colouring-matters in which there are not some members possessed of this peculiarity, and owing it to the same uniform cause. Still the group of the oxyketones, to which alizarine itself belongs, remains the true home of mordant-dyes, but this group has grown to-day into a very numerous and varied one. Mordant-dyes of every shade are to be found in it, and cotton is no longer the only fibre to which such dyes are applied. It is a fact worthy of notice, that amongst the many dyes of this class which we now possess and the constitution of which is fully established, there is not a small number, the molecule of which contains three, four, five, or even six hydroxyl groups. Yet this increase of auxochromic groups does not influence in the least the behaviour of these dyes to mordants; this is only governed by the two hydroxyl groups in ortho-position, and any other such group introduced into the molecule only changes the shade, not the characteristic chemical properties.

A greater variety still than by the achievements of modern synthetical work will come into this group of mordant-dyes by the progress of the elucidation of the constitution of the natural dye-stuffs occurring in roots, barks, and woods. A good many of them are still unsolved mysteries, but there can be no doubt that they owe, like alizarine, purpurine, and the other madder dye-stuffs,

their property of dyeing metallic mordants to the presence of hydroxyl groups in ortho-position in their molecule.

A very large and varied group of colouring-matters, which for a long time resisted all attempts at unravelling their constitution, are the safranines, eurhodines, oxazines, thionines, indulines, and other allied groups. They are now completely understood, and have been recognised as the amino- and oxy-derivatives of certain peculiar substances such as the azines and azonium-bases, the molecule of which possesses a ring-structure. Here no longer carbon atoms only form the closed chain, but nitrogen, oxygen, and even sulphur atoms participate in its structure and bring about the peculiar properties of the compounds. When this fact was at first ascertained it seemed sufficient for the explanation of the behaviour of such compounds as dyes. It was only somewhat later on that we recognised that in these classes of dye-stuffs especially a quinonoid structure is essential.

The greatest and most brilliant success of the chemistry of dye-stuffs is, however, the industrial synthesis of indigo. This offers so many points of general interest that I am sure to meet with your approval if I refer to it in some detail.

The indigo problem is one of the oldest problems of chemistry. When Baeyer took it up more than thirty years ago he found the ground well prepared by others who had worked before him. But his is the merit of having completely elucidated the constitution of this extraordinary product of nature. He and others have also shown various methods for the synthesis or artificial production of indigo. In the laboratories artificial indigo has been known for the last twenty years.

But in this case the scientific synthesis of a natural product proved to be by no means identical with the industrial one. Industrial methods can only enter into competition with nature if they work more economically than nature does. In the case of indigo there seemed to be little hope for fulfilling this condition. The most enthusiastic admirers of the modern synthetical industry could not help seeing that all evidence in our hands went against the probability of the practical synthesis of indigo, and just those who understood most of these things could least of all close their eyes to that fact. It could not be denied that every possible synthesis of indigo, those known as well as those which might still be expected, had to start from some aromatic derivative of benzene, containing one carbonic and one nitrogenous side-chain in ortho-position. Of all the products at our disposal which fulfil that condition, orthonitrotoluene is the most easily accessible. Now, taking it for granted that indigo could be prepared regularly and with good yields from orthonitrotoluene, there still remained that difficulty, that all the toluene produced in the world, even if we suppose that all the other uses to which this hydrocarbon is put at present could be suppressed, would not suffice for the production of the world's consumption of indigo.

If, under such circumstances, the industry of artificial dye-stuffs continued to work at the indigo problem, it did so more for the general interest attached to it, and with a view to securing some of the finer applications of indigo in printing, than in the hope of being able to compete with the natural product in the great consumption of vat dyeing. If, on the other hand, the indigo planters in the far East showed but small apprehension of the danger of which they were occasionally warned, we cannot blame them for it; they had no doubt taken the advice of competent people, and these had told them what was correct according to the knowledge of the time.

The final result has shown all the calculations of experts to be wrong, but in such a way that they, too, can surely not be blamed for the error they committed.

The process by which indigo is at present manufactured on a colossal scale by the Badische Anilin- und Soda-Fabrik in Ludwigshafen on the Rhine, is based on Heumann's synthesis of this most important dye-stuff,

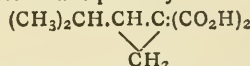
which consists in submitting phenylglycin to a fusion with caustic alkali. Phenylglycin is prepared by the action of monochloroacetic acid upon aniline. The yield of indigo obtained is a poor one, but it can be very much improved if, instead of phenylglycin, we take its orthocarbonic acid. In this we have again the presence of a nitrogenous and a carbonic side-chain in ortho-position. To prepare this acid we should have to start, according to the ordinary rules, from toluene, transforming it by a succession of operations. Thus we come again to toluene as a starting-point, and to the difficulty already explained.

There is, however, one somewhat abnormal process of preparing the same compound from phthalic acid. It consists in converting this into phthalimide, and treating the latter with sodium hypochlorite. By a somewhat complicated reaction, the nature of which need not be explained, one of the carboxyl groups of the phthalic acid is replaced by the amido group, anthranilic acid is formed, and this, if treated with monochloroacetic acid, yields phenylglycin-carbonic acid, which has proved so important for the manufacture of indigo. Now phthalic acid is prepared by a powerful oxidation of naphthalene, and naphthalene again is that constituent of coal-tar which is present in by far the largest quantity.

It is true that the process for transforming naphthalene into phthalic acid, which was the only one known at the time when all these facts were first recognised, gave very bad yields, and was at the same time costly. The whole indigo problem stood thus reduced to the problem of transforming naphthalene cheaply and economically into phthalic acid. This has been accomplished by the Badische Anilin- und Soda-Fabrik by heating naphthalene with fuming sulphuric acid in the presence of mercury salts. Torrents of sulphur dioxide escape, and the whole process can only be carried out properly if the means be given to convert this gas again into fuming sulphuric acid, which may be used again for treating fresh quantities of the hydrocarbon. The new sulphuric acid process of the Badische Anilin- und Soda-Fabrik has thus been of paramount importance for the working out of the indigo problem.

(To be continued).

Reaction of Sodium-malonate of Ethyl on the Dibromides, $C_nH_{2n}Br_2$.—V. Ipatief.—In the reaction of sodium-malonate of ethyl on bromide of isopropyl-ethylene, $(CH_3)_2CH \cdot CHBr \cdot CH_2Br$, we obtained the ether of a non-saturated acid, boiling at $122-132^\circ$ under 18 m.m. pressure; saponification gave a non-saturated bibasic acid with the composition $C_8H_{12}O_4$, soluble in benzene and chloroform, but less soluble in water, and fusing at $76-78^\circ$. This acid decolourises permanganate of potash; its formula is probably—



It is distinguished from its isomer, dimethylallylmalonic acid, $(CH_3)_2C:CH \cdot CH_2 \cdot CH(CO_2H)_2$, inasmuch as it is soluble in chloroform, and has a soluble salt of calcium and a silver salt more soluble in water. In the reaction of sodium-malonic ether on the bibromide in question, no carbide is formed, but there are traces of acetyltetracarboxylic ether. Thus, the dibromides in which the Br's are primary and secondary, behave with regard to the sodium-malonic ether differently to those in which one of the Br's is tertiary, and the other primary or secondary. With the bromide, $(CH_3)_2C(CH_2Br)_2$, the reaction takes in a different manner; it is necessary to heat for a long time, about 100 hours; a crystallised product is then formed, fusing at $105-105.5^\circ$, soluble in alkalis, from which it is precipitated by acids. This body decolourised permanganate of potash; by bromisation it gives a material fusible at $127-128^\circ$; its composition answers to the formula $C_7H_8O_4$. Its examination is not yet complete.—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 647.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, June 5th, 1902.

Prof. THORPE, C.B., F.R.S., Vice-President, in the Chair.

(Concluded from p. 12).

103. "Optically Active Esters of β -Ketonic and β -Aldehydic Acids. Part II. Menthyl Acetoacetate." By A. LAPWORTH and A. C. O. HANN.

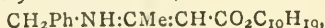
Menthyl acetoacetate may be obtained in small quantity by the action of sodium on menthyl acetate, but is far more easily prepared by heating menthol with ethyl acetoacetate until alcohol ceases to come off. These observations were made before the authors were aware that Cohn had prepared the ester by the latter process (*Monatsh.*, 1900, xxi., 200-204). As Cohn has since notified (*Ber.*, 1900, xxxiii., 734) that he had abandoned the work, with his concurrence the authors have resumed the study of this substance and its derivatives.

The compound may be obtained in large, lustrous, probably monoclinic prisms which the authors believe to represent the ketonic form. Its rotation in 2 per cent solution in benzene is initially about $[\alpha]_D = -61-62^\circ$, but slowly increases to about -68° , owing doubtless to partial conversion into the enolic form; similar changes are observed when it is dissolved in chloroform, light petroleum, and dry ethyl acetate. The duration of the change varies greatly with the purity of the solvent, as the compound is exceedingly sensitive to catalytic agents. As usual, all bases accelerate the change, and the mutarotation, unlike that of camphorquinonehydrazone and of nitrocamphor, is accelerated by traces of acids also. Equilibrium between the two forms appears to be attained almost at once in alcohol, practically no alteration of rotation with time being noticeable.

The copper derivative of the ester crystallises from alcohol in green prisms which contain alcohol; these rapidly become opaque, and finally have the melting-point $117-118^\circ$.

The ester readily affords a well-defined semicarbazide, $\text{NH}_2 \cdot \text{CO} \cdot \text{N}_2\text{H}_2 \cdot \text{CMe} : \text{CH} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, flat needles, m. p. $143-144^\circ$; in benzene $[\alpha]_D = -56.1^\circ$. The p-nitrophenylhydrazide, $\text{C}_6\text{H}_4\text{NO}_2 \cdot \text{N}_2\text{H}_2 \cdot \text{CMe} : \text{CH} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, brilliant prisms, m. p. $105-106^\circ$; in benzene $[\alpha]_D = -42.5^\circ$.

Menthyl β -aminocrotonate, $\text{NH}_2 \cdot \text{CMe} : \text{CH} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, prepared by the action of gaseous ammonia; forms large, transparent plates, m. p. $88-89^\circ$; in benzene $[\alpha]_D = -105.2^\circ$. Menthyl β -phenylaminocrotonate, $\text{NHPh} \cdot \text{CMe} : \text{CH} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, crystallises in flat, rectangular plates, m. p. $85-86^\circ$; it has $[\alpha]_D = -98.2^\circ$. Menthyl benzylaminocrotonate,—



crystallises in flat needles, m. p. $85-86^\circ$; in benzene $[\alpha]_D = -59.8^\circ$.

Menthyl C-benzoylacetoacetate, $\text{CHBzAc} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$, is an oil; in benzene $[\alpha]_D = -44.3^\circ$; its copper derivative forms slender needles, is sparingly soluble in most media, and melts at about 230° .

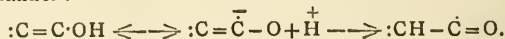
Neither the oxime, the isonitroso-, nor bromo-derivatives of the ester have yet been obtained in a pure condition.

The ester condenses readily with aldehydes, forming, in some cases, well crystallised compounds. Unlike ethyl acetoacetate, when condensed with benzaldehyde at the ordinary temperature by the aid of piperidine, it affords, for the most part, a monobenzylidene compound.

104. "The Mechanism of Simple Desmotropic Change." By A. LAPWORTH and A. C. O. HANN.

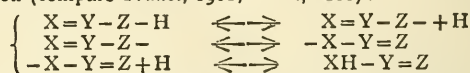
Brühl has advanced the hypothesis (*Ber.*, 1899, xxxii., 2329) that enols (which are weak acids and electrolytes)

are transformed into the isodynamic ketones, by a process which involves initial ionisation into hydrogen ions and organic ions or "residues," which may re-unite in two ways, so that finally the ketone is produced in this manner:—



He found, as he anticipated, that the velocity of transformation of enolic ethyl mesityloxideoxalate in solution into the ketonic form increases roughly with the dielectric constant of the medium.

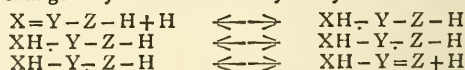
Although the principle here introduced appears quite reasonable, and more capable of experimental and theoretical development than any other yet suggested, it is clearly incomplete, since ketones, although apparently non-conductors, are known to exist in equilibrium with their conducting enolic forms, and the velocity of transformation must be far slower than the ionisation velocity. Since change of internal structure is necessary, and isomerisation appears to increase with ionisation, the authors think that Brühl's suggestion would lead to the following view of the processes involved in a keto-enol transformation (compare *Trans.*, 1901, lxxix., 1266):—



Here it appears necessary to assume that ketones themselves are very slightly ionised, which is consistent with the views of Thiele, Vorländer, and others. According to this view, bases should accelerate and acids retard the change, and the state of equilibrium should be independent of the catalytic agent, but dependent, not only on the two dissociation constants, but also on the velocities indicated in the second line. It is, in fact, perfectly consistent with the properties of certain isodynamic pairs, for example, nitro- and isonitro-camphor (Lowry, *Trans.*, 1899, lxxv., 221) and camphorquinonehydrazone.

However, the complete difference in behaviour of camphorquinonehydrazone and menthyl acetoacetate toward acids indicates that there are at least two classes of substances, and that more than one type of process may go on.

To account for the action of acids in accelerating the speed of migration of a hydrogen atom, in certain cases, on a principle similar to that proposed by Brühl, it seems necessary to assume that the compounds may react as bases. Since, as before, a change of structure is involved, the change may be conventionally analysed as follows:—



where the dot indicates the direction in which the "free affinity" of Y is temporarily disposed, a convention easily understood by reference to models.

The process thus represented requires an acceleration of the change by acids, and a final state of equilibrium independent of their presence.

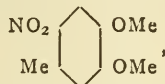
Clearly, a compound might react in either or possibly in both ways, according to the conditions. In nearly all cases observed, however, the first process would appear to go on, the latter being somewhat exceptional, at least as an important factor. Obviously, the state of equilibrium must be the same when attained by either process.

105. "Trimethylbrazilone." By W. H. PERKIN, jun.

During the course of a long series of experiments on the constitution of brazilin, it was shown (W. H. Perkin and A. W. Gilbody, *Proc.*, 1899, xv., 27) that trimethylbraziline, $\text{HO} \cdot \text{C}_{16}\text{H}_{10}\text{O}(\text{OMe})_3$, on oxidation with chromic acid, yields trimethylbrazilone, $\text{HO} \cdot \text{C}_{16}\text{H}_8\text{O}_2(\text{OMe}_3)$. It was also stated that nitric acid converts trimethylbrazilone into a substance crystallising in yellow needles, which dissolve in alkalis, forming an intense purple solution; this, on standing, yields besides β -methoxyxyalic acid $\text{MeO} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO}_2\text{H}$, two neutral substances

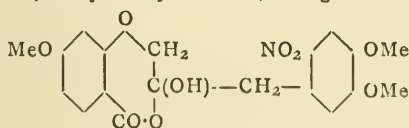
melting at 118° and 206° respectively. Since the yellow substance did not give the usual qualitative tests for nitrogen, it was at first thought that it did not contain this element; subsequent quantitative experiments, however, demonstrated the presence of nitrogen, and showed that the substance has the formula $C_{10}H_{10}O_9N$. It is proposed to name it *nitrohydroxydihydrotrimethylbrazilone*.

The two neutral substances having the melting-points 118° and 206° are probably isomeric, and have the formula $C_9H_{11}O_4N$, and as they each contain two methoxy-groups, they are apparently nitrodimethoxymethylbenzenes, the former (m. p. 118°) being probably identical with the compound—



which has already been prepared by H. Cousin (*Ann. Chim. Phys.*, 1898, [7], xlii., 480), and which melts at 117° . There is, however, a possibility that the very sparingly soluble substance of melting-point 206° has a higher molecular weight such as that represented by the formula $(C_9H_{10}NO_4)_2$.

When nitrohydroxydihydrotrimethylbrazilone is oxidised with permanganate, it yields 2-carboxy-5-methoxyphenoxyacetic acid, and since it also yields an acetyl compound, it is probably a lactone, having the formula—



or some formula closely allied to it.

The author has not yet concluded his experiments on this interesting nitro-compound, but finds it necessary to publish this short note because of a recent publication of Bollina, Kostanecki, and Tambor (*Ber.*, 1902, xxxv., 1675), which contains a description of some experiments on this compound.

The author hopes that these chemists will allow him, for a short time longer, the uninterrupted investigation of this substance.

PHYSICAL SOCIETY.

Ordinary Meeting, June 20th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

MR. G. F. HERBERT-SMITH exhibited the Three-Circle Goniometer recently constructed for the British Museum from his designs.

In this form of goniometer the advantages of the earlier forms are combined; as with the two-circle or theodolite goniometer, a crystal is only once adjusted during the whole of the observations, and as with the one-circle goniometer observations are made in zones, and full advantage may be taken of the zonal characters of crystals and of the simple formulæ depending thereon. The instrument is an improved form of a similar one designed by the exhibitor in 1899. In place of the usual telescope and collimator an auto-collimating telescope is employed, and a prism is placed before the object-glass so that the line of reference is horizontal and at right angles to the axis of the telescope. In this way it is possible to obtain a reflection from a face parallel to, and on the side of, the crystal towards the vertical circle, and measurements may be made in a zone across the end of the crystal by rotation of the horizontal circle only.

Prof. EVERETT asked whether the reflection was at normal incidence. If so, was not the light very much enfeebled?

Mr. APLEYARD drew attention to the method of reading

the scales by micrometer eye-pieces, thus saving the use of verniers.

Prof. PERRY suggested that the instrument should be made of nickel-steel alloy of low coefficient of expansion. This alloy is now manufactured in England, and is quite cheap.

Mr. HERBERT-SMITH, in reply to Prof. Everett, said that the image obtained at normal incidence was faint, but it was much more distinct than images obtained with other angles of incidence.

A paper "On the Heat Evolved or Absorbed when a Liquid is brought in contact with a finely-divided Solid," was read by Mr. G. J. PARKS.

Pouillet discovered the fact that when a powder is put into a liquid which does not exert any solvent or chemical action upon it, there is, in general, a rise of temperature. The objects of the present investigation were to obtain a relation between the quantity of heat evolved and the area of the surface exposed, to find the rate of variation of heat evolved with temperature, and to apply to the results the laws of thermodynamics. In making any experiment on the Pouillet effect it is essential that the powder should be perfectly dry, and that it should be at exactly the same temperature as the liquid. The precipitated silica, sand, or other substance to be experimented upon was heated to a dull red heat and placed in a bulb whilst still hot. The air was then exhausted, and the bulb sealed. In making an experiment the bulb containing the powder was broken under the surface of the water in a calorimeter, and the rise of temperature noted. The average diameter of the grains of powder used was obtained by measurement with a microscope, and on the assumption that the grains were spherical the surface of the mass of the powder used was calculated. From the results of his experiments the author states that when silica, sand, or glass is brought into contact with water at approximately constant temperature, the heat evolved is proportional to the area of the surface exposed by the solid, and the amount of heat developed per square centimetre is approximately 0.00105 calorie when the temperature is near 7° C. Assuming that the phenomenon of Pouillet is reversible, and that it is due to a pressure at the surface of the powder, the author has, by the application of the laws of thermodynamics and the results of his experiments, arrived at the conclusion that at 7° C. the surface-pressure of water and silica diminishes at the rate of 157 dynes per centimetre for an increase of temperature of 1° C. Experiments made at different temperatures indicate that the heat evolved is roughly proportional to the absolute temperature. Experiments were also made which showed a fall of temperature on putting a finely divided solid into mercury.

Prof. EVERETT said the research was a valuable contribution to our knowledge of the Pouillet effect. The results were consistent in showing a generation of heat to the amount of about one-thousandth of a therm per sq. cm. of increase of surface of contact between the water and the silica. He thought this heat must be due to diminution of volume in the water-film; for extension of area of a liquid film tended to produce cold. Cold was in fact produced by enlargement of the surface of mercury in the concluding experiments.

Mr. J. MACFARLANE GRAY said that the paper was to him peculiarly interesting, because satisfactory explanations of the phenomena described could be obtained by substituting the universal dynamic pressure of a corpuscular ether for the unthinkable universal attraction of matter. He gave an example to illustrate what he calls the metafilm at a surface, and pointed out that it is necessary to consider both the matter-volume and the meta-volume of bodies to get at the explanation of physical phenomena. In the author's experiments there is a diminution of meta-volume, and the ether produces heat equal to the product of the ether pressure and the volume of the cancelled metafilm, just as the heat of evaporation is reproduced when steam is condensed. The experi-

ments were to him not a surprise, but a confirmation of his views.

Mr. R. S. WHIPPLE said that the Pouillet effect could be shown by covering the bulb of a thermometer with muslin and putting it into a steriliser. On taking it out and immediately placing it in the mouth, there is a considerable rise of temperature. He had tried covering the bulb with dry muslin, and obtained a rise of 2° C. by putting the instrument into water.

Mr. J. H. GARDINER drew attention to the necessity of heating the powdered silica to red-heat in order to get rid of moisture. If possible, the silica should be heated in the actual tube and sealed up whilst hot.

A paper by Prof. R. W. WOOD, "*On a Remarkable Case of Uneven Distribution of Light in a Diffraction Grating Spectrum*," was read by the SECRETARY.

It is a well-known fact that in the spectra formed by diffraction-gratings the light is unevenly distributed, that is the total light in any one spectrum will not re-combine to form white light. The author has been examining a most remarkable grating in which the drop from maximum illumination to minimum occurs within a range of wavelengths not greater than the distance between the sodium-lines. In other words, the grating at a certain angle of incidence will show one of the D lines, and not the other. Experiments with polarised light have proved that these anomalies are only exhibited when the direction of vibration (electric vector) is at right angles to the ruling. The paper gives a detailed account of the appearance of the spectra at different angles of incidence when the grating is in air and when it is immersed in different liquids. It is shown that the phenomena are not due to interference between disturbances coming from widely separated lines, and the author suggests that the matter must be referred to the form of the groove.

A paper by Prof. R. W. WOOD, "*On the Electrical Resonance of Metal Particles for Light Waves*" (Second Communication), was read by the SECRETARY.

In a previous paper the author has shown that granular deposits of the alkali metals exhibit brilliant colours by transmitted light. These colours were referred provisionally to the electrical resonance of the minute particles for light waves. The present paper gives an account of experiments made with gold and silver films to determine whether the resonance is molecular, or whether it is an electrical vibration of metallic masses, smaller than the light waves, though of the same order of magnitude. Further investigations on the dispersion of the films and a more careful study with polarised light will doubtless throw light on the matter.

Prof. H. L. CALLENDAR showed a Simple Apparatus for Measuring the Mechanical Equivalent of Heat.

A cylindrical brass calorimeter is rotated by hand about a horizontal axis at a moderate speed. Unequal weights are suspended from the ends of a belt slung over the cylinder. Stability of equilibrium is secured by making the two halves of the belt of different materials and connecting the side having the smaller coefficient of friction to the larger weight. The weights are adjusted by trial to suit the friction of the belt, and may be varied within wide limits, provided that the ratio is kept nearly the same. The advantages of the methods are:—1. The friction is very nearly independent of the speed. 2. The balance is automatic; the belt immediately adjusts itself to any change of load or friction. 3. There is no change in the thermal capacity of the calorimeter with change of speed or load. 4. There is no pull or bearing-friction to introduce errors. 5. There are no forced vibrations, and no dashpot is required. 6. The actual torque may be measured statically if desired. The rise of temperature is observed by means of a bent platinum thermometer inserted through a hollow axle on one side. The external loss of heat can be eliminated by Rumford's compensation method, or by performing two experiments with different loads on the belt. The motion of the surface of the calorimeter eliminates

the effect of draughts and convection currents, so that the heat loss is much more regular than if the surface were at rest.

The Society then adjourned until October 24th, 1902.

NOTICES OF BOOKS.

Sewage Works Analysis. By GILBERT J. FOWLER, M.Sc. (Vict.), F.I.C., Superintendent and Chemist, Manchester Corporation Sewage Works. London: P. S. King and Son. New York: John Wiley and Sons. 1902. Pp. 135.

PROBABLY at no class of works is analysis of more importance than at those erected for the treatment and disposal of sewage. The work, moreover, like that at water-works, must be continuous, as any cessation in the necessary constant care and attention, without doubt would be followed quickly by pollution of the river or estuary into which the effluent is discharged.

The volume now before us gives an account of the methods of analysis in use in the laboratory of the Manchester Corporation Sewage Works; and, through the courtesy of Mr. Scudder, the author has also been able to include descriptions of some of the more important processes employed in the laboratory of the Mersey and Irwell Joint Committee.

In general, it may be stated that the Manchester methods are for the analysis of a large number of samples of sewage and effluents of the same general character, while the Joint Committee's methods are designed for cases where samples from different works have to be critically examined.

The book is divided into eight chapters and four tables. The first chapter deals generally with the chemical control of sewage purification processes. These processes may be broadly divided into two classes:—

- (a) Mechanical or disposal processes.
- (b) Biological or purification processes.

The first head includes such methods as the removal of garbage and detritus by catch-pits and screens, and the settling out of suspended matters in sedimentation tanks; certain chemicals are used, such as lime, sulphate of alumina, or lime and copperas, and eventually a clear effluent is left.

The biological processes are more modern than the former class just referred to. These processes make use of the micro-organisms originally present, or capable of development in the sewage, to entirely change the organic impurities in the sewage and convert them into harmless inorganic substances.

The remaining chapters deal with the estimation of the various constituents of sewage matter, and the elements generally present therein, such as ammonia, absorbed and dissolved oxygen, nitrates and nitrites, chlorine, acidity and alkalinity, iron compounds, &c., and the analysis of gases from the septic tank and from bacterial filters. The two latter analyses afford valuable information as to the progress of the respective processes.

Finally, there are a few pages of so-called useful tables of atomic weights, weights and measures on the metric system, some conversion tables, and a fairly good index. The book is well and clearly written, and will be useful in laboratories where this class of work is undertaken; it is also adorned with a number of full-page plates illustrating some of the special instruments employed in the work.

Great Britain, Her Finance and Commerce. Morning Post Souvenir Edition. London: The Morning Post. 1901. Pp. 606.

OWING to the failure of a certain person to fulfil his engagements with regard to a large number of advertise-

ments, obtained by the unauthorised use of the name of the *Morning Post*, the proprietor of that well-known paper determined to publish the projected volume at his own cost, thus giving those firms the advertisement they had paid for.

The volume is published for gratuitous distribution through the British Consuls, Exchanges, principal hotels, steamship companies, &c., in all parts of the world, and from a close examination of the book we are bound to admit that it is of far greater interest than most gratuitous literature we have come across at similar places.

There, are, of course, many advertisements, but at the same time there is much more space devoted to interesting and well illustrated articles on a variety of subjects; there are, in fact, forty such articles, each written by an expert. Among these we may call attention to "British Shipping," by Major Jones; "Electrical Industries," by Conrad Cooke; "By-Products from Coal," by Samuel Rideal; "Twentieth Century Sanitation," by J. Priestley; besides others on such diverse subjects as Cold Storage, Construction Material, Hats, Agriculture, Cycles, Locomotives, Chemical Manufactures, and Linen.

There are also a number of full-page plates illustrating the Houses of Parliament, the *Morning Post* Offices, and the town halls and principal buildings in most of our large cities.

The book is well printed on good paper and handsomely bound.

The Tokyo Imperial University Calendar, 2561-62 (1901-1902). Tokyo: Published by the University. 1902. Pp. 328.

Nothing shows better evidence of the enormous advance made by our "New Allies" during the past half century than the calendar now published yearly by the Tokyo University. In appearance it is almost the counterpart of the calendars issued by our own colleges, and apparently comprises all the subjects taught at home. With the exception of the final page the whole is printed in English and in English characters, and does great credit to those responsible for its production.

Practical Methods of Urine Analysis, for Chemists and Druggists, with Notes on the Composition of the Normal and Abnormal Renal Secretions. Second and Enlarged Edition. Published at the Office of the *Chemist and Druggist*, London; also Adelaide, Melbourne, Sydney, and New York. 1902. Pp. 88.

The present edition of this book covers about the same ground as the first, which was published in the year 1899, but it has been re-written to a great extent. It is primarily intended as a guide to chemists and druggists in a branch of work which is becoming more necessary to medical diagnosis; we cannot agree, however, with the editor that "no class of men is better fitted to fill this office than are pharmacists"; the business of a pharmacist is to dispense medicines and not to diagnose cases.

Still the book is a very useful one of its kind, and has been enlarged to the extent of thirty pages; it also includes a short formulary of reagents and processes, as well as much new matter. The index is three times the size of that in the first edition, which fact indicates that more care has been taken in its compilation as well as the extent of the revision the book has undergone.

Text-book of Physiological and Pathological Chemistry. By G. BUNGE. Translated by FLORENCE A. STARLING, and Edited by ERNEST H. STARLING. London: Kegan Paul, Trench, Trübner and Co., Ltd. 1902.

This text-book of pathological and physiological chemistry, intended for the use of physicians and students, is a translation, most ably performed, of the latest German edition. The style in which it is written is attractive and

stimulating, and cannot fail to inspire the beginner with interest. References to the original papers are fully given on all important or disputed points of the subject, so that the book may be made the basis of exhaustive studies of an advanced nature; great importance is rightly attached by the author to the student's referring constantly to the original literature, and drawing his own conclusions from it. The subject-matter is divided into twenty-nine lectures, arranged in such a way as to provide a complete course of physiological chemistry, and the editor has pointed out cases where Prof. Bunge's views differ from those of the majority of physiologists.

Naturlehre. ("Nature Study"). By Dr. ALOIS LANNER. Wien: Jos. Roth'sche Verlagsbuchhandlung. 1902.

THIS text-book of elementary natural science covers the German official syllabus of scientific teaching issued in February, 1900, and is adapted for the use of the higher classes in intermediate schools. It deals with the elements of mechanics, physics in all its branches, and chemistry, but it cannot be said that the spaces allotted to the various subjects are very evenly balanced. Some thirty pages only are devoted to the whole of chemistry; in these pages not only a brief review of the theory is given, but also an attempt is made at a detailed treatment of the inorganic elements and compounds, and organic chemistry. As might be expected, the result is the merest sketch of the subject. On the other hand, the theory of light is treated far more fully, the pages devoted to polarisation containing a specially good account of that phenomenon. Under Elementary Mechanics is included all that is usually found in a school text-book; only the minimum amount of mathematical knowledge is required in this section. In electricity and magnetism great stress is laid upon practical applications; in fact, this may be said to be a feature common to every section. The book concludes with brief outlines of astronomy and physical geography, but botany and zoology are omitted.

First Book of Qualitative Chemistry. By ALBERT B. PRESCOTT, Ph.D., and EUGENE C. SULLIVAN, Ph.D. New York: D. Van Nostrand Company. 1902.

THIS is the eleventh edition of a book first published in 1879, and has been entirely re-written by the authors. The object of the book is to familiarise the beginner with the present theories of water solution and the law of mass action, and at the same time provide a first course in qualitative analysis. Thus the student who works through the book will not only be conversant with the methods of separation of the most commonly occurring elements and be able to analyse mixtures of inorganic salts, but he will also be acquainted with the main features of the ionic theory, and modern notions concerning solubility and hydrolysis. The introductory sections vary extremely in difficulty. Thus, the rudimentary principles of chemical nomenclature and notation are fully explained, the student being presumably supposed to be ignorant of the most simple formulæ, while some of the sections are really stiff reading, and will very probably prove somewhat bewildering to the beginner. On the other hand, the suggested exercises on the metals of the various groups are most valuable; the advantage of always using solutions of known strength (generally 5 N) cannot be too strongly emphasised, and the tests for delicacy of precipitation should be very useful in encouraging accuracy of observation and manipulation.

Alloys of Cadmium and Magnesium.—O. Boudouard.—The alloys of cadmium and magnesium are all of a white colour more or less brilliant. It is difficult to obtain a perfectly polished surface for microscopic examination. They break if subjected to repeated hammering.—*Comptes Rendus*, cxxiv., No. 24.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 24, June 16, 1902.

Polymerisation and Heat of Formation of Zinc Oxide.—M. de Forcrand.—The numbers obtained by different investigators for the heat of formation of zinc oxide vary from 83.28 cal. to 88.20 cal., the variation being about 5 cal. The author re-investigates this matter in order to elucidate the constitution of the hydrates of zinc peroxide, which substances he has recently been examining. He finds, starting from solid zinc and oxygen gas, the heats of formation of the oxides form a series:—+80.29 cal., +82.98 cal., +84.30 cal., and +84.70 cal. It is thus seen that the series is an increasing one, and this can be explained if it is admitted that the oxide polymerises when it is heated, the reaction being exothermic. It is not reversible, and the oxide when heated to a bright red heat and then cooled gives the same number and preserves a stable state of polymerisation, even if cooled slowly and preserved for a long time. Such polymerisation evolves +4.41 cal.

Compounds of Sulphuretted Hydrogen with Anhydrous Aluminium Chloride.—E. Baud.—Wöhler showed that anhydrous aluminium chloride, when sublimed in a current of sulphuretted hydrogen, retains a certain quantity of this gas. The product obtained has never been analysed. The author therefore investigates this substance to find whether the sulphohydric compounds of aluminium chloride are comparable to hydrates or ammoniacal compounds. He finds that under the action of liquid hydrogen sulphide—(1) a compound, $\text{Al}_2\text{Cl}_6\cdot\text{H}_2\text{S}$, stable at ordinary temperatures, is formed; (2) a compound, $\text{Al}_2\text{Cl}_6\cdot 2\text{H}_2\text{S}$, which is dissociable towards -45° , is formed. It is possible that the solution of Al_2Cl_6 in liquid H_2S contains a compound still richer in sulphuretted hydrogen.

Isomerism in the Benzylidene-menthones, and Preparation of an α -Methyl- α' -isopropyl-adipic Acid Identical with Dihydrocamphoric Acid.—C. Martine.—From the oily products which are formed during the different methods of preparation of benzylidene-menthone which the author previously described, he now separates two compounds which apparently have a definite composition, as seen by their crystalline form and by their fusing-point, and which correspond to the composition of benzylidene-menthone. The one crystallises in tables fusing at 51° , is soluble in ether, alcohol, petrol ether, &c. In a 6 per cent solution of ethylic alcohol its rotatory power is $[\alpha]_D = -185.50$; its oxime is found in the form of fine needles fusing at 172° . The other compound, which was only obtained in small quantities, crystallises in long needles fusing at 47° . It is more soluble than the former compound in the same solvents. Its rotatory power under the same conditions is $[\alpha]_D = -258.5^\circ$. Its oxime has the same appearance as that of the body melting at 51° . This melts at 153° .

Pyromucic and Isopyromucic Acids. Action of Phosphorus Perchloride and Phosphoryl Chloride.—G. Chavanne.—The action of phosphorus perchloride on pyromucic acid was investigated by Liës-Bodart. He obtained a liquid boiling at 170° , forming the acid under the action of water, and giving an amide melting at 141 – 142° under the action of ammonia. The author repeats these experiments and arrives at the same results whether operating without a solvent or in chloroformic or ethereal solution. After complete purification the chloride appears in extremely refracting prisms melting at about 0° . He examines this product with regard to its action on water, alcohol, ammonia, aniline, and hydrazine hydrate. Pyromucic acid behaves as an acid with regard to phosphorus perchloride, the carboxyl group being replaced by COCl . Isopyromucic acid behaves in a totally different manner,

and is apparently not, strictly speaking, an acid like its isomer, but it seems to possess the properties of a body containing the phenolic or enolic function.

MISCELLANEOUS.

Action of Iodide of Ethyl on Nitrate of Silver.—E. Biron.—In the absence of any solvent, iodide of ethyl reacts energetically on nitrate of silver, giving $\text{C}_2\text{H}_5\text{NO}_3$ in almost theoretical amount, and disengaging about 10,000 cal. It is best to pour the $\text{C}_2\text{H}_5\text{I}$ drop by drop on the powdered nitrate of silver mixed with fine sand in a cooled flask. In the presence of solvents the results are different. With alcohol, as has already been shown by Nef, we obtain besides $\text{C}_2\text{H}_5\text{NO}$, ordinary ether, $(\text{C}_2\text{H}_5)_2\text{O}$, and nitric acid. In the presence of water there are formed $\text{C}_2\text{H}_5\text{NO}_3$, $\text{C}_2\text{H}_5\text{OH}$, and HNO_3 . Nef explained the production of $(\text{C}_2\text{H}_5\text{O})_2\text{O}$ by the formation of a product of transitory dissociation, $\text{CH}_3\cdot\text{CH}$, which unites with the HNO_3 and the $\text{C}_2\text{H}_5\text{OH}$, giving $\text{NO}_3\text{C}_2\text{H}_5$ and $(\text{C}_2\text{H}_5)_2\text{O}$; but this explanation cannot be admitted as it presupposes a unimolecular reaction, while the measurements of the speeds show that the action of the nitrate of silver on $\text{C}_2\text{H}_5\text{I}$ and on $\text{C}_2\text{H}_5\text{Br}$ are bimolecular reactions. The formation of ether, $(\text{C}_2\text{H}_5)_2\text{O}$, and of products of saponification of nitrate of ethyl in much greater quantities than those which result from the saponification of $\text{NO}_3\text{C}_2\text{H}_5$ by water, are attributed by the author to the action of alcohol and water on nitrate of ethyl in the nascent state.—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 667.

Oxidation of some Non-saturated Acids by a Mixture of Sulphuric Acid and Persulphate of Ammonium.—A. A. Albitzky.—In a previous paper (*Bull. Soc. Chim.*, vol. xxii., p. 695) the author showed that by the successive action of HClO and KOH on oleic, elaidic, erusic, and brassidic acids he obtained dioxysearic and dioxybenic acids different from those obtained by direct oxidation by means of permanganate of potash in alkaline solution, or by the action of Ag_2O on the dibromides of the non-saturated acids. In the present research, not yet finished, the author has sought for the conditions which influence the production of one or the other of the stereoisomer dioxyacids; he has found that the results are different according as the oxidising medium is acid or alkaline. By using a mixture of concentrated sulphuric acid and $\text{S}_2\text{O}_8(\text{NH}_4)_2$ he obtained:—With oleic acid, dioxysearic acid fusible at 99.5° ; with elaidic acid, a dioxyacid fusible at 136.5° ; with erusic acid, dioxybenic acid fusible at 99 – 100° ; and with brassidic acid, a dioxyacid fusible at 131 – 133° .—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 640.

THE
DAVY FARADAY RESEARCH LABORATORY
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Superintendent of the Laboratory:

Dr. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

This Laboratory was founded by Dr. LUDWIG MOND, F.R.S., as a Memorial of Davy and Faraday, for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

MICHAELMAS TERM.—Monday, October 6, to Saturday, December 13.

LENT TERM.—Monday, January 5, to Saturday, April 4.

EASTER TERM.—Monday, April 27, to Saturday, July 25.

Full information and forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

To prevent delay Candidates ought to send in their applications for admission during the course of the Term preceding that in which they wish to enter.

THE CHEMICAL NEWS

VOL. LXXXVI., No. 2225.

NINTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1901.*

By F. W. CLARKE.

THE year 1901 has not been very prolific in researches upon atomic weights, at least so far as actual publications would seem to indicate. A fair amount of work, however, is announced from various sources, and doubtless it will appear in print during 1902. The investigations of current date are summarised in the following pages.

Nitrogen.

Scott (*Journ. Chem. Soc.*, 1901, lxxix., 147) has carefully re-determined the ratios between ammonium bromide and silver. The silver was purified by various methods, and each experiment is cited with the proper details upon this point. The ammonium bromide was prepared from hydrobromic acid, with ammonia from different sources. It was brilliantly white, and remained so upon heating to 180°, whereas that used by Stas in his investigations became greyish. All weights were reduced to a vacuum, and calculations were made with $\text{Ag} = 107.93$. Results as follows, but for details the original paper should be consulted:—

Weight NH_4Br .	Weight Ag.	Molecular weight NH_4Br .
4.89631	5.39380	97.975
2.45925	2.70914	97.972
3.29478	3.62928	97.982
4.46957	4.92273	97.994
4.20661	4.63303	97.996
4.23664	4.66644	97.989
4.31464	4.75175	98.001
6.19233	6.82047	97.990
8.77664	9.66608	97.999
10.47233	11.53416	97.994
4.91997	5.41834	98.0028
5.00442	5.51164	97.997
5.17914	5.70390	98.000
4.84099	5.33177	97.995
5.10677	5.62515	97.984

Rejecting the first three experiments, in which the bromide was slightly acid, Scott's mean value for the molecular weight of NH_4Br is 97.995. Stas found 98.032, and Scott supposes that his salt may have contained traces of platinum, whence the greyness which appeared on heating.

As a further check on the determinations Scott collected and weighed the silver bromide produced, and so determined anew the ratio between Ag and AgBr. Data as follows:—

Weight Ag.	Weight AgBr.	Ratio AgBr to 100 Ag.
6.82315	11.87733	174.074
9.66809	16.82816	174.059 (a)
5.41906	9.43315	174.0735
5.51258	9.59596	174.074
5.70686	9.93346	174.062
5.33191	9.28093	174.064
5.62572	9.79254	174.067

(a) 174.090 when corrected for a known impurity.

Stas' value for this ratio is 174.080.

Two additional experiments were made upon the ratio between ammonium chloride and silver.

Weight NH_4Cl .	Weight Ag.	Molecular weight NH_4Cl .
4.78257	9.64484	53.519
5.51744	11.12810	53.513

In still another experiment connected with these two, the silver chloride was weighed. 4.7850 NH_4Cl gave 12.82048 AgCl. Hence $\text{NH}_4\text{Cl} = 53.5164$. Stas' value is 53.532. Further investigations are promised; but until they are complete Scott regards it as premature to compute the atomic weight of nitrogen from these data. As they stand they give:—

From the bromide	$\text{NH}_4 = 18.040$
From the chloride	$\text{NH}_4 = 18.059$

Calcium.

The atomic weight of calcium has been re-determined by Hinrichsen (*Zeit. Phys. Chem.*, xxxix., 311). The purest Iceland spar was ignited, and the ratio so determined between CaCO_3 and CaO. A correction is applied for 0.032 per cent of Fe_2O_3 , found by analysis, and assumed to represent FeCO_3 in the original mineral. Weights were reduced to a vacuum, and calculations were made with $\text{O} = 16$ and $\text{C} = 12$. The data are as follows, all corrections applied:—

Weight CaCO_3 .	Weight CaO.	Atomic weight Ca.
30.72157	17.22354	40.144
32.77791	18.37587	40.141
34.45625	19.31698	40.142
33.36885	18.70723	40.141
Sum, 131.32458	73.62462	40.142

Herzfeld's determinations of the atomic weight of calcium, cited in the report of last year, have been reproduced in the *Berichte* (vol. xxxiv., p. 559), and so made accessible to the general reader.

Arsenic.

Somewhat elaborate determinations of the atomic weight of arsenic have been made by Ebaugh (Doctoral Thesis, University of Pennsylvania, 1901) under the guidance of Edgar F. Smith. First, silver arsenate was converted into silver chloride by heating in hydrochloric acid gas. All weights were reduced to a vacuum. The results are as follows, with $\text{O} = 16$, $\text{Cl} = 35.45$, and $\text{Ag} = 107.92$.

Weight Ag_3AsO_4 .	Weight AgCl.	Atomic weight As.
0.23182	0.21547	74.987
0.47996	0.44615	74.944
0.52521	0.48820	74.956
0.80173	0.74517	74.996
0.94782	0.88083	75.061
1.02047	0.94830	75.083
1.03558	0.96258	74.974
1.05462	0.98014	75.033

Mean 75.004

The silver chloride from seven of these experiments was next reduced by heating in hydrogen. The silver contained in the arsenate was thus determined, giving the following data:—

Weight Ag_3AsO_4 .	Weight Ag.	Atomic weight As.
0.23182	0.162175	75.027
0.47996	0.33583	74.950
0.52521	0.367525	74.907
0.80173	0.50099	74.936
0.94782	0.66318	74.959
1.02047	0.71400	74.964
1.05462	0.73771	75.082

Mean 74.975

* *Journal of the American Chemical Society*, vol. xxiv., No. 3.

Experiments upon the conversion of silver arsenate into bromide were unsatisfactory. The conversion of lead arsenate into lead chloride gave good results, however, as follows:—Calculated with $Pb=206.92$.

Weight $Pb_3As_2O_8$.	Weight $PbCl_2$.	Atomic weight As.
0.38152	0.35381	74.988
0.436197	0.40449	75.016
0.57218	0.53065	74.964
0.60085	0.55717	75.020
0.74123	0.68736	75.010
0.77107	0.71494	75.067
0.88282	0.81858	75.054
0.97779	0.90674	75.054
Mean		75.022

Three more determinations, based upon the conversion of lead arsenate into lead bromide by heating in gaseous hydrobromic acid, were also successful. Calculated with $Br=79.95$.

Weight $Pb_3As_2O_8$.	Weight $PbBr_2$.	Atomic weight As.
0.59704	0.73092	75.066
0.61712	0.75567	74.967
0.65799	0.80569	74.980
Mean		75.004

The general mean of all twenty-six determinations is—
 $As = 75.008$.

Various other methods of determination were attempted, but unsuccessfully.

Antimony.

Friend and Smith (*Journ. Am. Chem. Soc.*, 1901, xxiii., 502) have applied a new method to the determination of the atomic weight of antimony. Potassium tartrantimonite (tartar emetic) was heated in dry hydrochloric acid gas, the final residue of the operation being potassium chloride. All weights were reduced to a vacuum. The results were as follows, when $H=1.008$, $C=12$, $K=39.11$, and $Cl=35.45$.

Weight of salt.	Weight KCl.	Atomic weight Sb.
1.19481	0.27539	120.345
1.57004	0.36186	120.359
2.00912	0.46307	120.351
2.04253	0.47073	120.379
2.16646	0.49935	120.341
2.25558	0.51982	120.385
2.61255	0.60215	120.350
2.95272	0.68064	120.311

Mean 120.353

This value approximates to those found by Schneider and by Cooke from their studies of antimony trisulphide.

(To be continued).

SPECIFIC WEIGHTS OF VARIOUS TIMBERS.

By E. G. CLAYTON, F.I.C., F.C.S.

DETERMINATIONS have been made of the relative densities (water = 1) of the following varieties of seasoned timber. The weighed blocks had been accurately sawn and planed to as nearly as possible identical cubic dimensions, namely, $8 \times 3 \times 2$ inches.

Of course, the figures do not express the actual specific gravities of the woody substance deprived of water, which would approach 1.2 to 1.5, but "the sum of the weight of the solid matter with that of the water contained in it, and of the air of the pores" (Groves and Thorp, "Chemical Technology," 1889, i., 6).

The specimens had been carefully chosen for a small museum of economic botany, and were thoroughly representative; they are named in the list in the order of

their densities, and roughly classified as soft, hard, or medium woods.

Genus and species of tree.	Ordinary name of tree or wood.	Relative density (water=1)	Nature of wood.
<i>Pinus strobus</i>	Quebec or yellow pine	0.433	Soft
<i>Populus fastigiata</i> ..	Lombardy poplar	0.452	"
<i>Abies excelsa</i> (Nor-way or European spruce fir), varie- ties of	Yellow deal (1)..	0.452	"
	Yellow deal (2)..	0.471	"
	White deal ..	0.471	"
<i>Abies nigra</i>	Yellow deal (3)..	0.490	"
	American spruce fir	0.509	"
<i>Abies Douglasii</i> ..	Oregon or Doug- las pine	0.529	"
<i>Tilia Europæa</i> ..	Lime or linden..	0.548	"
<i>Populus alba</i>	Abele or white poplar	0.558	"
<i>Juglans regia</i>	Walnut	0.625	Medium
<i>Ulmus campestris</i> ..	Elm	0.625	Hard
<i>Larix Europæa</i> ..	Larch	0.625	Medium
<i>Quercus robur</i> (Ped-unculate)	British oak ..	0.635	Hard
<i>Pinus Australis</i> ..	Southern or pitch pine	0.654	Soft
<i>Quercus robur</i> (Ses-siliflora)	Austrian oak ..	0.663	Hard
<i>Prunus cerasus</i> ..	Cherry	0.673	Medium
<i>Betula alba</i>	Birch	0.673	"
<i>Quercus cerris</i> ..	Turkey oak ..	0.673	Hard
<i>Fraxinus excelsior</i> ..	Ash	0.683	Medium
<i>Swietenia mahogoni</i>	Honduras ma- hogany	0.683	Hard
<i>Robinia pseud-acacia</i>	Acacia	0.692	Medium
<i>Pinus sylvestris</i> ..	Scotch fir	0.702	Soft
<i>Pinus sylvestris</i> ..	Memel fir	0.711	"
<i>Fagus sylvatica</i> ..	Beech.. ..	0.740	Hard
<i>Nectandra rodiaei</i> ..	Greenheart ..	0.759	"

Chemical Laboratory,
32, Holborn Viaduct, E.C., July 8, 1902.

COMPOUNDS OF CHLORIDE OF BISMUTH WITH THE ORGANIC BASES.

By L. VANINO and O. HAUSER.

CHLORIDE of bismuth is dissolved without change in acetone, and the solution treated with organic bases gives precipitates. In the case of aniline and other amino-benzenic bases we obtain amorphous deposits, slightly nitrated and badly defined, but with other bases we obtain well characterised crystalline precipitates which may be, according to the conditions, compounds of $BiCl_3$ either with the hydrochlorate of the base or with the free base.

Chloride of Bismuth and Quinolein, $BiCl_3.C_9H_7N$.—An excess of the base poured into the acetonetic solution of $BiCl_3$ gives a thick crystalline mass, slightly soluble in acetone. The salt is hardly changed by water; if in the preparation the chloride of barium contains a little free acid the salt is contaminated with the double chloride, $BiCl_3.2(C_9H_7N.HCl)$, which is also slightly soluble.

Iodide of Bismuth and Quinolein, $BiI_3.C_9H_7N$.—The preceding salt added to a boiling aqueous solution of iodide of potassium gives a deep red liquor, which, after cooling, deposits a red precipitate of the corresponding iodide.

Chloride of Bismuth and Hydrochlorate of Quinolein, $BiCl_3.C_9H_7N.HCl$.—The salt $BiCl_3.C_9H_7N$ dissolves easily in dilute hydrochloric acid, and on evaporation the solution gives crystals of the double chloride.

Chloride of Bismuth and Pyridine, $2BiCl_3.3C_5H_5N$.—This has been already described by Montemartini (*Gazz. Chim.*, 1900, p. 493), but is obtained as easily in the form

of a white powder by the author's method; it is non-hygroscopic, slightly changed by water, and decomposed by heat into chloride of bismuth and pyridine.

Iodide of Bismuth and Pyridine, $\text{BiI}_3 \cdot \text{C}_5\text{H}_5\text{N}$.—The same method of preparation is used as for quinolein. It occurs as a deep red powder, finely crystalline; it is slightly soluble in warm alcohol or in a solution of iodide of potassium; it is deposited from this latter solution, on cooling, in small needles.

Chloride of Bismuth and Hydrochlorate of Pyridine, $2\text{BiCl}_3 \cdot 3(\text{C}_5\text{H}_5\text{N} \cdot \text{HCl})$.—The compound of chloride of bismuth and pyridine dissolves in dilute hydrochloric acid, and the solution gives, on evaporation, beautiful needles of the double salt; this salt is decomposed by water, giving a deposit of BiOCl .

Chloride of Bismuth and α -Naphthylamine, $3\text{BiCl}_3 \cdot 2\text{C}_{10}\text{H}_7\text{NH}_2$.—A concentrated solution of α -naphthylamine in acetone, poured in excess into an acetic solution of chloride of bismuth, furnishes a white crystalline precipitate, slightly soluble in dilute hydrochloric acid and in acetone; it is decomposed by water, and also by an excess of hydrochloric acid; in this latter case BiCl_3 and $\text{C}_{10}\text{H}_7\text{NH}_2 \cdot \text{HCl}$ are formed.

Iodide of Bismuth and α -Naphthylamine, $\text{BiI}_3 \cdot 2\text{C}_{10}\text{H}_7\text{NH}_2$.—Proceed in the same manner as with pyridine and quinolein; the blood-red liquor is filtered hot to separate a deep brown resin, then evaporated in the desiccator, where it gives long deep red needles arranged in bunches; this body cannot be washed without decomposition, and, further, the return is very small.—*Berichte*, vol. xxxiv., p. 416.

RECENT DEVELOPMENTS IN COLOURING-MATTERS.*

By Geheimrath Professor OTTO N. WITT, Ph.D. F.C.S., of Berlin.

(Concluded from p. 16).

SOME of the older synthetical methods of producing indigo are so easy and rapid that they can easily be shown as a lecture experiment. If, for instance, we add a caustic potash solution to a solution of orthonitrobenzoic aldehyde in acetone, indigo is formed at once and settles out in dark blue crystalline flakes (Exp. IX.). The synthesis now in practical use is a little more delicate in its execution, but there are certain modifications of it which are rapid enough to be shown in a lecture experiment (Exp. X.).

The action of the alkali on the phenylglycin-carbonic acid does not at once produce indigo, a colourless derivative of the dye, indoxylcarbonic acid, or rather its potash salt, is formed at first; but if we dissolve this in hot water, and introduce a current of air, it is at once, and with a quantitative yield, transformed into indigo which settles out in the shape of a crystalline deposit of infinitely fine division. This is collected in filter-presses, and delivered into commerce in the shape of a paste or a powder.

The industrial synthesis of indigo is extremely interesting, because it is a triumph not wholly due to chemical science. Science has shown the way to success, but it was quite unable to clear away the difficulties arising from practical and economic considerations. Here the representatives of our great industry had to advance independently and on paths for which theoretical knowledge could not serve them as a guide. Unlimited praise and admiration is certainly due to them for the masterly way in which they grappled with colossal difficulties, and for the courage with which they staked millions on the realisation of one great idea.

At the same time we cannot help feeling some regret for the indigo planters in the far East, who, after enjoying

more than a century of easy prosperity, see now that more serious times are in store for them. They see the day coming when the indigo plantations will disappear, in the same way in which the madder fields of Avignon have vanished. But we are consoled by the knowledge that, especially for India, the time has already come, which has been so vividly described by Sir William Crookes, in one of his addresses to the British Association; as the future in store, sooner or later, for all humanity, the time when bread begins to be scarce. It seems to me that any one who, by bringing about some great commercial revolution such as we have seen in the indigo trade, causes land in India to become free for the growing of rice and other cereals, renders a great service to large numbers of poor natives, and need therefore not be blamed for lessening to some extent the prosperity of a class of people who have had an unusually good opportunity of accumulating wealth in the past.

It is a strange fact, that with indigo the history of the fight of the madder root against artificial alizarine is almost literally repeated in spite of the great difference of original conditions in the two cases. Madder was a product containing at its best only 4 per cent of actual colouring matter; the rest was useless fibre and obnoxious impurities which greatly hampered the dyer in his work. Alizarine, entering into competition with this natural product, was, on the contrary, the colouring matter in a pure state, and therefore not only cheaper but also much easier in its application. Indigo, such as we receive it from India and Java, is a manufactured article, the best qualities of which contain 59, 60, or even 70 per cent of pure dye-stuffs, besides impurities which have always been considered as perfectly harmless. Thus the artificial product did not seem to have much scope for improvement as far as the quality came into consideration. Here again we have committed a mistake. We know now that the impurities are not harmless, and that the blues dyed with artificial indigo are quite as superior in brightness and purity of shade to those obtained with natural indigo, as alizarine reds were to madder reds. This has, however, not always proved to be an advantage for the manufacturers of artificial indigo. The world does not ask for bright indigo shades, and a good many prejudices in that respect had to be overcome before artificial indigo was admitted as a legitimate substitute for the natural product in some of its most important applications. Yet a simple consideration will show that it is always easy to deteriorate the brilliancy of a dyed shade, whereas no art of the dyer will suffice to produce brilliant shades on textile fabrics with dye-stuffs that carry their share of dirty admixtures within them.

In its application to the fibre, indigo is perhaps the most remarkable of all dye-stuffs, for it is the principal representative of that extraordinary class of colouring-matters which must be applied by the vat process. This process, which consists in first reducing the dye-stuff into a leuco-compound before applying it to the fibre, on which the original colouring-matter is formed again by the action of the oxygen of the air, seems to have nothing in common with the ordinary dyeing processes. If, however, we consider it more closely, we come to the conclusion that vat colours are a class of dye-stuffs in which the functions of dyeing and of selective absorption of light are distributed on two different forms of the substance, one of which contains two atoms of hydrogen more in its molecule than the other.

This theory is supported to some extent by the fact that, what we are pleased to call leuco-compounds are in the majority of cases by no means colourless. Indigo-white itself is not white but yellow in its alkaline solution which we call a vat. Other vat-dyes have leuco-compounds which are even more strongly coloured. Thus the leuco-compound of indanthrene, a beautiful new colouring-matter, is blue like indanthrene itself; flavanthrene, a yellow dye-stuff, which has not yet left the laboratory of its inventor, has a blue leuco-compound. One may say,

* A Lecture delivered at the Royal Institution of Great Britain, Friday, March 21, 1902.

that with all vat-colours the real dye-stuff is the leuco-compound which is afterwards, when once fixed on the fibre, transformed into a pigment by the oxidising influence of the air.

In 1825 Faraday discovered, in this very house, benzene; the original specimen, prepared by his own hands, is before you. We look upon it reverently, like on a sacred relic bequeathed to us by a master-mind. But what a development has sprung from this first attempt to unravel the mysteries of the aromatic series! Our science as well as our industry have been revolutionised by the investigation of the derivatives of benzene, and the world has been embellished by the gay and brilliant dyes of which it is the mother-substance. The study of the chemistry of these dye-stuffs has become a domain of science which, for variety and fascination, can hardly be surpassed by any other. The deeper we penetrate into it the more it proves an inexhaustible mine of the most subtle scientific thought, yet one which never loses touch with practical life; it is interesting alike to the philosophical mind that wishes to revel in the wonderful perfection and order of nature, and to the philanthropic spirit which rejoices in seeing many thousands of hands occupied and princely fortunes produced by the utilisation of what was only a short time ago a refuse and an encumbrance. It teaches a lesson even to those who are not attached to science and apt to consider it as a kind of pastime for people who lack ability for practical life. For they cannot help seeing that, in this case, the most intricate science has led to something eminently practical, commensurate to a standard which, though unknown to the Bureau International des Poids et Mesures, is to some people the only reliable one, viz., the one of £ s. d.

I am afraid that the high praise which I feel justified in bestowing on what has been the favourite pursuit of my life is not fully substantiated by the contents of this lecture. The subject which I had to treat is so vast, that all I have been able to say is nothing but a sketch or a programme of what would require a long series of lectures if full justice were to be done to it. My one excuse for attempting to sketch, in the short space of one hour, so vast a subject, is the place in which I had the honour to speak. An audience that has been addressed more than once by the pioneers of the chemistry of dye-stuffs, by Faraday, Hofmann, William Perkin, and others, could, from one of the Epigones, not have looked for more than a few notes and additions.

NOTES ON IRON ANALYSIS.

By GEORGE T. DOUGHERTY, Chicago.

Complete Evolution Method for Sulphur in Iron.

IT has been a matter of knowledge among many of us since about ten or fifteen years ago, though it has never been promulgated in text-books issued to date, that the evolution method frequently fails to give the full amount of sulphur present in samples of pig- or cast-iron, the deficiency ranging from 0.005 up to 0.025 per cent, which is the maximum that I have obtained in my individual experience. Various unsuccessful attempts have been made to overcome this defect of the method, in order to avoid resorting to the slow and tedious gravimetric oxidation method. Among them has been the use of hot dilute hydrochloric acid instead of cold for starting the decomposition, the treatment of the insoluble residue after evolution for any additional sulphur, and the addition of an arbitrary correction factor of 0.010 to 0.020 to the per cent obtained by direct titration. This is the custom in many places, a practice which involves a serious element of uncertainty when it comes to the question of accepting or rejecting a car lot of pig-metal bought on the specification of not to exceed 0.030 or 0.050 per cent of sulphur,

as the case may be. The insoluble residue rarely yields on examination enough sulphur to account for the shortage. Most of the lost sulphur is supposably of the organic or mercaptan series, which is not absorbable in the alkali solution.

Recently there came to my notice a method proposed by Walters and Miller of annealing iron drillings in a porcelain boat in a porcelain or nickel tube in a current of natural gas or some non-oxidising gas, previous to solution in the evolution flask. The principle of the method, together with the closely agreeing analyses submitted by the authors in corroboration, appeared attractive to me, but the mode of application required would put it out of the way of many crowded laboratories which may not care to instal such a bulky apparatus. My mind chanced to hit on trying a covered porcelain crucible in its stead, and I have found it to work like a charm, no current of any kind of gas being necessary, but only a piece of filter-paper loosely laid on top of the drillings in order to maintain a reducing atmosphere during the operation of igniting for fifteen minutes. I first tried wrapping the drillings in filter-paper, and found it would require at least one-half hour's ignition to get out the maximum results. If, however, the drillings are placed direct in the porcelain crucible and one-half of a 9 c.c. filter-paper is laid loosely on top of the mass, fifteen minutes' strong ignition is sufficient. The "adjustable" type of Bunsen burner sold for gasoline gas will give the requisite strong temperature with coal-gas. Heavily graphitic drillings barely need the presence of paper to prevent oxidation, but it is a safe policy to use it on all kinds of iron samples. After the ignition the drillings will be found to have slightly set or caked together, but are easily disintegrated and transferred without loss into the evolution flask. I use 50 c.c. of 1 to 1 hydrochloric acid on 5 grms. of drillings and absorb the H_2S evolved in 17 c.c. of caustic potash solution (350 grms. of Merck's purified stick potash in 2 litres) in a Will and Varrentrapp nitrogen bulb, which is admirably adapted to prevent back suction as well as to insure a double bubbling of the gas. This amount of potash solution, after diluting to the usual volume of 400 c.c. in a No. 4 Griffin beaker, and acidifying with 20 c.c. strong hydrochloric acid, usually takes up 0.1 to 0.35 c.c. of standard iodine solution in a blank test, and of course this must always be deducted. Standardise the iodine solution with a standard steel, whose sulphur contents have been determined by two or more gravimetric oxidation analyses, preferably of over 0.050 per cent sulphur. The iodine solution is made up by dissolving 17.715 grms. of pure iodine in a 50 c.c. solution of 30 grms. of potassium iodide in a beaker, and after all is dissolved by shaking, dilute to 5 litres; each c.c. of it will be found to equal 0.0005 gm. sulphur or 0.010 per cent sulphur when calculated on 5 grms. of steel run through as above. Verify each fresh iodine solution, or whenever in doubt, by running the standard steel through under similar conditions as for regular work. In gravimetric oxidation work on standard or special samples, the addition of 20 c.c. bromine water to 60 or 80 c.c. of the usual aqua regia will effect the complete oxidation of all the sulphur present, which is not usually possible with the simple aqua regia; only one evaporation is necessary.

Below I give a memorandum of my various experiments in this complete evolution method. The three standard cast-irons, B, C, and D, were furnished by the Standardising Bureau of American Foundrymen's Association, with its official analyses of same. The two Lebanon pigs are coppery, 0.8 to 1.25 per cent copper; the gravimetric sulphur percentages given of each were determined by myself.

Standard Iron B.

Official analysis .. $\left\{ \begin{array}{l} 0.038 \text{ per cent sulphur by evolution method.} \\ 0.056 \text{ per cent sulphur by oxidation method.} \end{array} \right.$

	Evolution method. Per cent.
Not ignited previously	0.041
Wrapped in filter-paper and ignited thirty minutes	0.059
Wrapped in filter-paper and ignited fifteen minutes	0.053
Ignited fifteen minutes without any paper at all	0.049
Ignited fifteen minutes, paper on top of drillings	0.052
	0.055
	0.057
	0.058
	0.057
Standard Iron C.	
Official analysis ..	0.059 per cent sulphur by evolution method.
	0.076 per cent sulphur by oxidation method.

	Evolution method. Per cent.
Not ignited previously	0.060
Wrapped in filter-paper and ignited thirty minutes	0.076
Ignited fifteen minutes, paper on top of drillings	0.076
	0.079
	0.076

Standard Iron D.	
Official analysis ..	0.024 per cent by evolution method.
	0.031 per cent by oxidation method.

	Evolution method. Per cent.
Not ignited previously	0.022
Ignited fifteen minutes, paper above drillings	0.031
	0.030

Lebanon Pig, 1.	
Oxidation method	0.046
Evolution without previous ignition	0.020
Evolution after one-half hour's ignition ..	0.043

Lebanon Pig, 2.	
Oxidation method	0.032
Evolution without previous ignition	0.010
Evolution after one-half hour's ignition ..	0.030

Stewart Pig.	
Oxidation method	0.011
Evolution without previous ignition	0.003
Evolution after fifteen minutes' ignition ..	0.009

There always appears an uneven mass of "scum" on the surface of the liquid when iron drillings not previously ignited have been dissolved in the evolution flask. But when the drillings treated had been ignited before the solution would have a smooth surface and be as free of scum as that of steels. In the case of the three cast-iron standards, B, C, and D, the solution after ignition of the drillings takes place very quickly and almost instantaneously; but the Lebanon pigs after ignition require a rather longer time for complete solution than when not previously ignited. I use 20 c.c. water + 35 c.c. strong HCl on Lebanon pigs on account of their peculiar or coppery nature, when ordinary irons require only 25 c.c. water + 25 c.c. strong HCl.

Determination of Graphite by Direct Weight.

One grm. of drillings is treated with 60 c.c. of nitric acid, 1.13 specific gravity, in a No. 2 Griffin beaker; gentle heat is applied for about thirty minutes, or until no more nitrous fumes come off; then boil hard for about five minutes. Weigh previously a Gooch crucible and a disk of Swedish No. 0 filtering-paper cut to about the size of the bottom of the Gooch crucible and just previously dried for one hour at 115 degrees C., weighing the disk after three or five minutes in the desiccator, for it is sometimes

aggravatingly hygroscopic. Stir the liquid just before filtering it into the paper disk fitted in the Gooch crucible under suction. Wash in this order:—Once with diluted nitric acid, thrice with hot water, twice with hot 10 to 15 per cent KHO solution, thrice with hot water, twice with hot dilute hydrochloric acid, thrice with hot water, once with alcohol, and once with ether or 87 degrees test gasoline.

Dry the Gooch crucible and contents for one hour at 115 to 120 degrees C., and weigh after five minutes in the desiccator (1), open the crucible and ignite until nothing black remains, and weigh again (2).

1. Increase of weight over combined tares of Gooch crucible and paper disk equals graphitic matter plus silica, &c.

2. Increase of weight over tare of crucible equals silica or mineral matter.

1—2 equals graphitic matter. Graphitic matter multiplied by 0.96 equals amount of true graphite.

The object of stirring the liquid just before filtering is to prevent occasional clogging of the filter by the gelatinised silica. This, together with the washing with KHO, removes all the necessity for introducing any hydrofluoric acid, as is used by several chemists. Hydrofluoric acid does not decompose or remove any carbide insoluble in simple dilute nitric acid, as KHO does. Hydrofluoric acid, whenever used, usually causes irregular final results. It will be necessary to wash the graphitic residue with KHO, not only to remove silica, but also to decompose the small quantity of insoluble carbide, which will be shown by the deep brown liquid running out of the filter on application of KHO. When the silica is all but eliminated in this manner graphite will be vastly easier and quicker to burn up. I do not recommend asbestos for filtering and burning graphite on for direct weighing, for two reasons:—

1. The burning of graphite on an asbestos filter, since it is out of contact with the red-hot metal of the crucible, is a very difficult and tedious operation in any crucible.

2. Asbestos, even when previously purified by acids and ignited, is, contrary to general expectations, slightly but appreciably volatile at the temperature of the blast-lamp or "adjustable" Bunsen, which temperature is necessary to burn up graphite. I have determined this fact by many experiments on different lots of asbestos.

The use of a Gooch crucible with a paper disk for filtering and weighing graphite and washing, as above recommended, and applying the factor for 0.96 are points of the method which will largely remedy objections heretofore urged against the method of direct weight for graphite. This method professes to give commercially accurate results, though not quite equal in scientific accuracy to the regular combustion process most carefully performed.

Continual Diminution of Graphite in Much Used Drillings.

Dr. P. W. Shimer, in *Transactions of American Institute of Mining Engineers*, vol. xlv., recommends that for determining graphite in cast-iron the drillings be made wet with alcohol to mix and weigh out for analysis to prevent segregations and irregularities in results. I have since found out a startling fact—that if alcohol be not used in mixing the drillings the per cent of graphite (and total carbon also) will be constantly lowered little by little whenever the drillings are poured out of the container, mixed over and weighed out for any determination of that or other elements. Also, a serious loss in graphite will be suffered if drillings of cast- or pig-iron are powdered and sifted, as is done by many chemists, though with the laudable intention of securing a thoroughly homogeneous sample.

To illustrate the extent of loss in graphite contents in dry samples of iron drillings I submit here below the official analyses of standardised iron drillings A and D supplied by the Standardising Bureau of American Foundrymen's Association when freshly prepared, and my

own determinations (by combustion) after the contents of the bottles containing those two samples have been three-fourths or four-fifths used up :—

		Graphite when new.	Graphite after three-fourths has been used up.
		Per cent.	Per cent.
A		3'11	2'12
D		2'80	2'16

It is up to the Standardisation Bureau of the American Foundrymen's Association to supply its carbon standards only after mixing with alcohol, and fill the bottles with alcohol-moist drillings.

The probable reason for the constant loss of graphite in dry samples when much used is the low gravity of the graphite as compared with the rest of the iron, and its tendency to separate as fine dust and go off in the air whenever disturbed.

Recovery of Old Copper Solutions for Carbon Determinations.

Copper potassium chloride itself is not more expensive than other C. P. reagents usually used, by the pound, but as so much more of it is required per determination than other reagents are required for the estimation of other elements, it will form quite an item of expense when very many carbon determinations are made through that reagent. One pound of it will be used up in making a comparatively few carbon determinations, about 40 to 50 grms. being required for each determination. It will therefore be found economical to retreat or "revivify" old copper solutions with a view to re-using them for other carbon determinations.

The following plan has been adopted by me after various experiments with excellent results :—To 7 grms. of potassium chlorate already in a 16-ounce flask add 400 of the old copper potassium chloride solution and 40 c.c. strong hydrochloric acid. Heat to boiling, and boil strongly for five or ten minutes. When cool filter through asbestos and it will be ready for re-use. A slight odour of free chlorine will not be hurtful. One-half of the 40 c.c. strong hydrochloric acid used above is necessary to re-dissolve and keep in solution the re-oxidised iron salts, and the other half is calculated to supply the usual 5 per cent of free acid to the solution. After revivifying five or six times it will be advantageous to throw them away, they having then become so nearly saturated with salts as to cause slow filtering on some steels.

Manganese in Iron and Steel.

Standard potassium permanganate solution, 3'90 grms. of the salt in 2 litres of water. Each c.c. equals 0'0010 gm. manganese, or 0'20 per cent of manganese when 1 gm. of sample is weighed out and treated, and one-half of the resultant solution is titrated.

The method :—Treat 1 gm. of drillings with 20 c.c. nitric acid of 1'13 specific gravity for cast-iron, or 15 c.c. nitric acid of 1'20 specific gravity for steel in a No. 2 Griffin beaker. Heat and boil until very low down in the beaker and the bulging centre of the bottom of the beaker almost shows up. Cool and dilute a little with water; transfer with rinsings into a 300 or 400 c.c. volumetric flask. Add emulsion of zinc oxide from a bottle, part by part, shaking the flask all the time, until the iron precipitates stiffly, then add a little more zinc oxide and shake vigorously, the precipitate showing a slight whitish tinge; and fill up with water to the mark. Pour all into a No. 3 Griffin beaker, and stir well with a glass rod. Let settle for a few minutes, and pour the rather (not excessively) milky supernatant liquid carefully into a 150 or 200 c.c. volumetric flask (according as it has been from a 300 or 400 c.c. volumetric flask) up to the delivery mark. One-half of either 300 or 400 c.c. will represent $\frac{1}{2}$ gm. of sample. Pour it from the 150 to 200 c.c. flask into a 16-ounce ordinary flask; bring it to a boil, and titrate as usual with standard permanganate solution. If the burette reads 4'2

c.c. then $4'2 \times 0'2$ equals 0'84 per cent Mn. I have a standard steel of 0'75 per cent manganese which has been determined gravimetrically, with which I check up the standard permanganate solution when freshly made up or whenever in doubt of it, or to determine any correction needed in the routine work. For example, the permanganate solution in use at present would show on test with the standard steel 0'77 per cent manganese instead of 0'75; therefore, I deduct 0'02 from all the results obtained by titration with this permanganate solution.

The advantages of this modified Volhard method are :—

1. No evaporation with sulphuric acid is necessary.
2. This obviates any necessity for filtering off the iron.
3. It is desirable to have a slight excess of zinc oxide present when ready for titrating, as indicated by the moderately milky appearance of the liquid, as it increases the sharpness and permanency of the end reaction in titrating.

In case one is troubled with over-titrations from having to deal with samples running unusually high in manganese (over 2 per cent), and widely differing in high manganese contents not approximately known, it would be practicable to titrate back, as is done in the Gay-Lussac method of assaying silver bullion, with a standard solution of manganous chloride, which may be prepared by evaporating the proportion of 15 c.c. standard permanganate solution down to 3 or 4 c.c., adding a few drops of hydrochloric acid, and boiling as long as chlorine comes off; then neutralising with zinc oxide, and diluting to 10 c.c., when 1 c.c. equals 1 c.c. permanganate solution. This method if preparing a standard manganous chloride solution is due to Dubois and Mixer. If these gentlemen were correct in giving proportions of permanganate solution to convert into a standard manganous chloride solution, I would simplify and save time and labour of evaporating down the very dilute standard permanganate solution by taking of the dry permanganate salt equivalent to 1500 c.c. of standard permanganate solution (2000 : 1500 :: 5'90 : x = 2'975 grms.), dissolving it in 50 c.c. water in a No. 3 Griffin beaker, treating as directed, and finally diluting to 1000 c.c., when 1 c.c. equals 1 c.c. permanganate.—*The Iron Age*, May 8, 1902.

EXPERIMENTAL RESEARCHES ON THE CONSTITUTION OF CRYSTALS.*

By A. E. TUTTON, B.Sc., F.R.S., F.C.S.

EXPERIMENTAL work in connection with the study of crystals offers attractions of a more than usually fascinating kind. For, in the first place, crystals themselves are such wonderfully beautiful objects; they are, indeed, unquestionably the most beautiful of all the inanimate productions of Nature. It is even doubtful whether we are right in considering them inanimate, for the force of crystallisation, though it may lie dormant for thousands of years, is ever ready, when a suitable environment offers, to re-assert itself. In the second place, the study of crystals involves the investigation of that most exquisite of all the forms of energy, light—that extraordinary effect of wave-motion in the ethereal all-pervading medium, which we now believe to be due to an exceedingly rapid, periodic, oscillating change in the electrical condition of the atoms and molecules of the incandescent light-giving source.

We will allow the beam of light from an electric lantern to fall on this cluster of diamonds, carbon in its most exquisite crystalline form. The diamonds are arranged, as you see, in the shape of a crown, and were generously lent for this lecture by Mr. Streeter. You observe a magnificent play of light waves rippling towards you in every variety of colour and scintillation. The object of the experiment is that you may distinguish the two distinct

* A Lecture delivered at the Royal Institution of Great Britain, Friday, May 2, 1902.

types of emanation, namely, exterior reflections of white light from the facets and coloured rays due to penetration of the light into the interior structure of the diamonds, and subsequent refraction and reflection outwards again. The former kind you observe best in the innumerable images in white light of the carbon points of the lanterns, reflected on the ceiling and screen.

It is by the determination of the direction of the exterior reflections that we are enabled to ascertain the wonderfully regular angular relations of the various faces of the crystals; and it is by the study of the light which has penetrated that we gain the best information concerning the internal structure.

We shall consider this evening some of the results of a study of the crystals of certain series of definitely related chemical salts. There has been a great want of correlated work of this kind, having for its definite object the elucidation of the relationship between the chemical composition of a crystallised substance and the peculiar type of symmetry which it exhibits.

The salts which have, up to the present, been studied, are the sulphates and selenates of the alkali metals potassium, rubidium, and caesium, which crystallise in the rhombic system of symmetry; and thirty members of the well-known monoclinic series of double sulphates and selenates, containing one of the three alkali-metals just mentioned, another metal of the magnesium or iron type, and six molecules of water of crystallisation.

The research had two main objects. First, to discover the effect of replacing one alkali-metal by another; and second, the effect of replacing the lighter element, sulphur, contained in the acid radicle of the salt, by the heavier element, selenium. The three metals, potassium, rubidium, and caesium, belong strictly to the same family of chemical elements, according to the now famous periodic classification of Newlands and Mendeleeff. They are the most electro-positive metals known, and the weights of their atoms are related in a most interesting manner, that of rubidium being the mean of the atomic weights of potassium and caesium. It was, therefore, to be expected that any difference of form or properties brought about by the replacement of any one of these metals by another would be as great as could ever be produced by a change of this kind, and it might be hoped would be adequately great to enable a true idea of its character to be obtained. The very fact that no differences in the angles of the crystals of so-called isomorphous salts had, up to the commencement of this work, been detected with certainty, shows how very small, at most, such differences must be. It will also be evident that for such a research only the most perfectly formed and homogeneous of crystals must be employed. It is a primary essential that the faces of the crystals shall yield perfect images of the signal-slit of the goniometer, and in order that this may be so they must be absolutely plain surfaces. Indeed, if one may be forgiven a slight equivocation in the spelling of a word, the ladies present may be interested to hear that the beauty of crystals lies in the planeness of their faces.

The mode of measuring the angles between crystal faces on the goniometer, and at the same time the difficulty offered by imperfect faces, may be illustrated with the aid of this large crystal of quartz. It is mounted upon one of the actual goniometers employed in the work, but the size of the crystal is enormously greater than those actually used in the research, which rarely exceeded the size of a pin's head. Such small crystals are much more free from distortion than larger ones.

You now see on the screen the image of the goniometer signal-slit reflected from one of the faces of the quartz crystal. This image is an irreproachable one, the face reflecting it being truly plane. Its narrow part is capable of accurate adjustment to a vertical cross-wire. On rotating the crystal so as to bring the image from the next face, of the particular zone which has been previously adjusted, into the field, you observe that this also is a

very good image, but much weaker than the other. This is simply because it is derived from a much smaller face, but the face is quite plane. The next image you see is a bad one, being not only a multiple image, but distorted. Such an image would be quite useless for our purpose. Thus, on rotating round the whole zone—for it is one of the geometrical properties of crystals that the faces lie in zones—we find that some images are good and some are bad. In the case of very small crystals it generally happens that the greater number of images afforded by the faces are either one thing or the other, and crystals must be selected yielding the maximum of good images.

The first result of importance that has been brought to light is that, with regard to each series of salts, there is an interesting relationship between the general exterior character—or habit, as the crystallographer terms it—of any triplet of salts containing potassium, rubidium, and caesium respectively.

We will see on the screen, for instance, the configurations of the three double salts, potassium zinc sulphate, rubidium zinc sulphate, and caesium zinc sulphate. The same planes are present in all, but very differently developed. In the potassium salt the shape is determined by the large development of the prism zone (β faces), and the large flat end faces of the basal plane, c . The caesium salt, on the other hand, exhibits a prismatic habit formed by the faces of the clinodome, g , and the basal plane c is reduced to a strip. Intermediate between these two types comes the rubidium salt, and this is the case with the rubidium salt of every one of the sixteen triplets examined.

Hence the habit clearly follows the order of the atomic weights of the alkali metals.

The next general result arrived at is, that small angular differences between the faces have been established, but they rarely amount to a degree in magnitude. And what is of even more interest is, that the faces of every rubidium salt are inclined to each other at intermediate angles to those of the potassium and caesium salts.

This important fact may be illustrated by the vacuum-tube model on the table, which has been specially constructed to emphasise the point. The three crystal outlines represent sections through one of the principal planes of the alkaline sulphates or selenates. The outer one represents the outline of caesium sulphate or selenate, the middle one that of the rubidium salt, and the inner one a section of the potassium salt. The intermediate inclination of the domal faces will be clearly apparent. This is only one of some sixty angles which have been examined, and all show the same beautiful progression in the order of the atomic weights.

In the case of the principal angle of the monoclinic series, which determines the inclination of the inclined axis characteristic of that system of symmetry, the change of angle is directly proportional to the change in atomic weight.

Before concluding what may be said about the exterior morphology, reference may be made to one other fact, which follows from that just referred to and from the results of careful determinations of the specific gravity of the salts. The latter enables one to arrive at the molecular volume, which in the case of salts belonging to the same series does actually represent the relative volume of the chemical molecules. The size of the molecules of the rubidium salt was in every case found to be intermediate between the sizes of the molecules of the potassium and caesium salts. By combining these molecular volumes with the lengths of the crystallographical axes as afforded by the angular measurements, it has been possible to determine the relative dimensions, in the three directions of space, of each chemical molecule.

This was preceded by a proof, which has been confirmed by Dr. Fock, of Berlin, from an entirely different point of view, that the unit of the crystal structure in these salts was identical with the chemical molecule, and was not an aggregate of such,

The result has been to show that the sizes, or at any rate the distances apart from centre to centre, of the chemical molecules in the three rectangular directions of space are intermediate in the case of every rubidium salt. Thus the directional dimensions of the molecules, like the angles of the crystal structure, follow the order of the atomic weights of the alkali metals.

This fact is clearly exhibited in exaggerated fashion by the model, and it will be observed that the intermediate position of the rubidium salt is somewhat nearer to that of the potassium salt than to that of the caesium salt.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 18th, 1902.

Prof. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

MESSRS. Russell, Lattey, Ionides, Haas, and Heaton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Guy Dunstan Ricketts, Sir John Cass Technical Institute, E.C.; Edgar Stansfield, B.Sc., Technical College, Sunderland; Thomas Edward Wallis, 78, Essex Road, Islington, N.

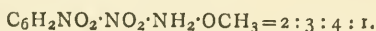
The PRESIDENT announced that the Council that afternoon had decided that the Ordinary Meetings of the Society for the ensuing session should be held, as far as possible, alternately, on Wednesdays at 5.30 p.m., and Thursdays at 8 p.m.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—James Handby Ball, B.Sc.; Edwin Thomas Holman Bucknell; Bryce Cudleigh Burt, B.Sc.; Arthur Crozier Claudet; William Thomas Clough; Henry Wilson Davis; Percy J. Ferris; Edgar William Foll; Francis E. Francis, B.Sc., Ph.D.; John Longsdon Garle; Alexander Gow, B.Sc.; Thomas B. Hallowell; Archie Cecil Osborn Hann; Walter Ernest Harrison; George Herbert Leader, B.Sc.; Charles B. Lessner; James Butler Moody; Thomas Henry Moore; Sinnott Valentine O'Connor; Percy Philip Phillips, Ph.D.; George Paton Pollitt, Ph.D.; William E. F. Powney; Herbert Purton; Stephen Jamieson Ralph; Edwin Ralphs; Prafulla Chandra Ray, D.Sc.; Harold James Roast; William Pearson Skerthchy; William C. S. Stanger; Hector Stewart; John William Wells; Joseph West; Edward J. Wheeler.

Of the following papers, those marked * were read:—

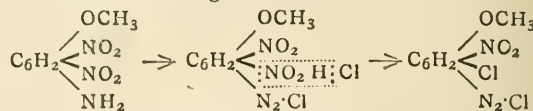
*106. "Elimination of a Nitro-group on Diazotisation. Dinitro *p*-anisidine." By R. MELDOLA and J. V. EYRE.

Dinitro-*p*-anisidine, obtained by nitrating acet-*p* anisidine and hydrolysing the acetyl derivative, was shown by the authors to have the constitution—

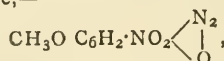


This compound, on diazotisation in acetic acid in presence of sulphuric or nitric acid, behaves normally, and forms a dinitrodiazonium salt, which on heating with alcohol gives dinitroanisole, $\text{C}_6\text{H}_3\cdot\text{NO}_2\cdot\text{NO}_2\cdot\text{OCH}_3=2:3:1$, of m. p. 119°. The dinitrodiazonium salts combine with alkaline β -naphthol in the ordinary way to form the azo compound, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\beta$. When diazotised in the presence of hydrochloric or acetic acid, one of the nitro-groups is eliminated as in the case of dinitro-*o*-anisidine (*Trans.*, 1900, lxxvii., 1172; *Proc.*, 1901, xvii., 131; *Trans.*, 1901, lxxix., 1076). The authors showed that it is the 3-nitro group, that is, the group which is *ortho* with respect to the diazonium group, which is thus eliminated. The product, when hydrochloric acid

is used, contains chlorine in place of the 3-nitro-group, and is formed according to the scheme:—



No diazoxide appears to be formed in this case, but the replacement of the nitro-group by chlorine takes place at once at the ordinary temperature. The chloronitrodiazonium salt, when boiled with alcohol, with or without the addition of alkali, gives chloronitroanisole, $\text{C}_6\text{H}_3\cdot\text{Cl}\cdot\text{NO}_2\cdot\text{OCH}_3=3:2:1$. The same diazonium salt, on combination with alkaline β -naphthol, gives the azo compound, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_2\text{Cl}\cdot\text{NO}_2\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\beta$. When diazotised in the presence of acetic acid alone, the NO_2 group is replaced by hydroxyl, and the diazonium salt combines with β -naphthol to form the hydroxyazo-compound, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_2\cdot\text{NO}_2\cdot\text{OH}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}\beta$. In this case, a diazoxide,—



may be formed as an intermediate product, but this has not yet been isolated.

The displacing of the nitro-group in the two dinitro-anisidines now investigated tends to show that the elimination of this group follows the *ortho*-*para* law, and experiments for the purpose of testing this conclusion will be undertaken in due course.

*107. "Preliminary Notice of some New Derivatives of Pinene and other Terpenes." By W. A. TILDEN and H. BURROWS.

Pinene nitrosochloride is remarkable as being the only known compound containing the elements of pinene from which that hydrocarbon may be regenerated. The addition of one molecule of hydrogen chloride to pinene gives the familiar monohydrochloride (artificial camphor, m. p. 128°), from which, by withdrawal of hydrogen chloride, camphene, and not pinene, results. The addition of two molecules of hydrogen chloride to pinene gives rise to dipentene dihydrochloride (m. p. 50°), from which, by removal of two molecules of hydrogen chloride, a mixture of liquid isomerides of pinene is obtained. On the other hand, when pinene combines with nitrosylchloride, a compound is formed which contains a nitroso-group. This is indicated by the fact that it is capable of reacting with aniline to yield a diazotised product, leaving a hydrocarbon which is apparently identical with pinene, though optically inactive (Wallach, *Ann.*, 1889, ccliii., 132; 1890, cclviii., 344).

The authors have repeated this experiment, and although the reaction is not so simple as they were led to infer from Wallach's account of it, they have verified the fact that the recovered hydrocarbon combines readily with nitrosylchloride, forming a nitrosochloride which melts at 110°, and from which a benzylnitrolamine melting at 125° was obtained. The corresponding compounds formed from ordinary dextro-pinene melt at 103° and 122–123° respectively (Wallach). The fact that this recovered pinene is optically inactive but not resolvable into two optical isomerides has not attracted the attention it deserves. If optically inactive pinene really possesses the same constitution as active pinene, this would imply the existence in the molecule of two asymmetric carbon atoms similarly combined. The formulæ given by Wallach, Wagner, and other chemists are therefore inadequate to explain the facts.

In the hope of getting some new light on the problem, attempts have been made to produce new derivatives of the hydrocarbon by adding carbon in various forms to the unsaturated part of the molecule, with the idea of obtaining acids or other compounds of determinable constitution. Several methods have been tested in a pre-

liminary way, but at present only one has met with success.

When pinene nitroschloride is gently heated with an equivalent quantity of potassium cyanide in the presence of 90 per cent alcohol, a compound having the composition of pinene nitrosocyanide is formed amounting to about 40 per cent of the nitroschloride employed. The viscous by-products have not been completely examined. The cyanide is a crystalline compound which forms large prisms, of which the melting-point is 171° . On analysis, the compound gave 14.47 per cent of nitrogen, $C_{10}H_{16}NOCN$, requiring 14.58 per cent. It dissolves readily in alcohol, ether, acetic acid, and toluene, but very sparingly in light petroleum, and it is practically insoluble in water.

The constitution of this nitrosocyanide is at present an unsettled question. It is unaltered by boiling with 30 per cent alcoholic potash for several hours. On the other hand, it is completely destroyed with formation of uncrystallisable products when heated with dilute sulphuric acid or with hydrochloric acid, either in alcoholic solution or in glacial acetic acid at 100° . It is therefore doubtful whether the compound is a nitrile. There are, however, other cases on record of nitriles which resist the action of alkalis, and the question is still under investigation.

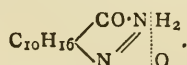
By digesting the cyanide with alcoholic potash and methyl iodide, a methyl derivative is produced which is distinguished by the readiness with which it forms large, colourless, prismatic crystals. The melting-point of this compound is 67° , and it contains 13.64 per cent of nitrogen, $C_{10}H_{15}CH_3NO \cdot CN$ requiring 13.60 per cent.

The action of reducing agents on the cyanide is rather remarkable. Three methods were successively employed, namely, (1) the action of sodium on a boiling solution of the cyanide in amyl alcohol, (2) the action of sodium on a boiling solution in ethyl alcohol, and (3) the action of zinc in the presence of alcohol and hydrochloric acid. In the reductions with sodium, some ammonia was evolved, and a cyanide was produced in considerable quantity, together with an almost quantitative yield of pinylamine.

The acid reducing agent produced practically no change, but when zinc dust and an alkaline solution were employed ammonia was evolved, and on steam distillation an oil of camphoraceous odour passed over.

A small quantity of a second crystalline, but not basic, compound, not yet investigated, was produced in both cases, and was extracted from the alkaline residue.

Pinene nitrosocyanide dissolves in concentrated sulphuric acid without coloration but with evolution of considerable heat. The solution, when diluted with water, yields the unchanged nitrosocyanide, but when the solution in sulphuric acid is digested at about 100° for an hour or two, the addition of water does not cause an immediate precipitate. On allowing the liquid to stand, a new compound is deposited in tufts of crystals, which, after re-crystallisation from alcohol, appear in the form of well defined plates which melt and decompose at about 220° . It is soluble in aqueous potash, and, somewhat strangely, also in hydrochloric acid. This compound contains 14.38 per cent of nitrogen, which corresponds closely with the amount required either by a polymerised product, $(C_{10}H_{16}NO \cdot CN)_n$, or by the product which would result from the formation of the corresponding acid amide and the subsequent elimination of water, thus:—



This is, however, a subject for further investigation.

Pinene nitrosocyanide, placed in contact with warm nitric acid (sp. gr. 1.4), liquefies but does not dissolve, while a small quantity of nitrous gas is evolved. In a few minutes, the reaction seems to be complete, effervescence ceases, and on pouring the whole into cold water, a solid is precipitated which crystallises readily from alcohol in colourless prisms. This compound is insoluble in aqueous

alkali. It melts with decomposition at 105° . Analysis gave 16.30 per cent of nitrogen. The formula of a mononitrosocyanide, $C_{10}H_{16}NO_2 \cdot CN$, requires 13.46, while that of a dinitrosocyanide, $C_{10}H_{15}(NO_2)_2 \cdot CN$, requires 16.60 per cent of nitrogen. It is probable, therefore, that the nitroso-group is oxidised, and nitration occurs at the same time.

An attempt to produce a nitrosocyanide from limonene nitroschloride gave a liquid product which is awaiting further investigation. Terpinene nitrosate is also expected to yield corresponding products.

With regard to the hydrochlorides obtainable from pinene, the monohydrochloride (m. p. 128°) refused to react under any circumstances with either cyanide of potassium or of silver. An alcoholic solution of dipentene dihydrochloride digested with potassium cyanide in the cold for fourteen days gave the liquid monohydrochloride, $C_{10}H_{16}HCl$, and the latter by continuing the action of the cyanide at about 120° , gave very pure terpinene, which was identified by its boiling-point (181°) and by the production of the characteristic crystalline nitrosate.

*108. "The Colour Changes Exhibited by the Chlorides of Cobalt and some other Metals from the Standpoint of the Theory of Electro-affinity." By F. G. DONNAN and H. BASSETT, jun.

The colour changes exhibited by aqueous and alcoholic solutions of the chlorides of cobalt, copper, and ferric iron on variation of temperature or dilution, or on the addition of various chlorides, such as those of hydrogen, calcium, magnesium, zinc, mercury, are shown to be largely due to the formation or dissociation of complex anions containing a metallic atom in association with chlorine. Evidence was brought forward to show that the dehydration theory is inadequate to explain the observed phenomena. Experiments on the motion of boundaries between different liquid layers on the passage of an electric current point to the existence of complex negative ions. Thus, in the case of cobalt chloride, the blue solutions travel towards the anode, the red solutions towards the cathode. Further experiments on the combination between cobalt and other chlorides in aqueous and alcoholic solutions admit of explanation on the above hypothesis.

*109. "The Stereochemical Formulæ of Benzene." By J. E. MARSH.

The author discussed the objections to the stereocentric formulæ of benzene brought forward by Graebe (*Ber.*, 1902, xxxv., 526), and pointed out that, according to the latter, rings identical in structure, which their properties do not admit of, would be assigned to benzene and naphthalene. The author considers that all the eight stereocentric formulæ are possible for benzene and its derivatives; that orthophthalic acid would have the *trans*-centric form, in which case it could form an anhydride, though the meta-acid could not, since the hexahydro-ortho-acid alone forms an anhydride in the *trans*-form. Thus, proximity of groups alone would not account for the formation of anhydrides, nor of carbonates and methylene ethers of dihydric phenols. Further, the absence of optically active compounds is accounted for if we regard the Kekulé formula as a labile form of the *cis*-centric, for the Kekulé model can close in two ways to form *cis*-centric formulæ, one being the optical image of the other.

With regard to substitution, those compounds which yield meta-derivatives contain an oxidisable group, whilst those which yield ortho- and para-derivatives contain a reducible group. In the former case, the repulsion of hydrogen leads to the *trans*-centric form with production of meta-derivatives. In the latter case, the attraction of hydrogen to the group leads to *cis*-centric hydrogen in the ortho- and para-positions. Bamberger's dicentric formula for naphthalene was also criticised, as it appears stereochemically impossible, and is not in accord with the constitution of allied hydrocarbons.

*110. "An Accurate Method of Determining the Compressibility of Vapours." By B. D. STEELE, D.Sc.

In the course of an investigation with Prof. Ramsay, it became necessary to determine, with a high degree of accuracy, the compressibility of certain vapours at low pressures. The apparatus employed consists of a combination of volume apparatus and pressure gauge, so constructed as to be capable of being contained together in a glass jacket which can be maintained at a constant temperature. The pressure is measured by setting two surfaces of mercury to carefully ground glass points the difference in level between which is known. The volume is obtained by weighing the mercury entering or leaving the apparatus.

Experiments with the vapours of benzene and ether have been made in the apparatus, and curves obtained showing the variation of PV with P for pressures varying from 40 to 200 m.m.

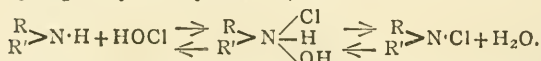
*111. "A New Type of Substituted Nitrogen Chlorides." By F. D. CHATTAWAY.

No substituted nitrogen chlorides known up to the present have three negative groups attached to the nitrogen. All contain at least one hydrocarbon residue.

Such a series of compounds of the type—



where R and R' are acyl groups, is yielded by the diacyl amides. These, when treated with hypochlorous acid or, under certain conditions, with chlorine, have their imino-hydrogen replaced by chlorine, thus:—



The diacyl nitrogen chlorides are colourless, well-crystallised compounds which show the typical behaviour of substances having halogen attached to nitrogen.

Dibenzoyl Nitrogen Chloride, $\begin{array}{c} C_6H_5 \cdot CO \\ C_6H_5 \cdot CO \end{array} > N \cdot Cl$.—In order to obtain this compound, dibenzamide, prepared by the action of fuming sulphuric acid and phosphorus pentoxide on benzonitrile, was dissolved in acetic acid. To the solution, an excess of a strong solution of bleaching powder was added. Chlorine was vigorously evolved, and a yellow oil separated. Chloroform was added, and the whole well shaken for a few minutes. The chloroform solution was then run off, washed with water, and finally with a dilute solution of potassium bicarbonate, dried over fused calcium chloride, and the solvent evaporated at a low temperature in a rapid current of dry air. The nitrogen chloride crystallised out as a white solid (m. p. 89°), readily soluble in chloroform and in benzene, but sparingly in petroleum. It crystallises from a mixture of chloroform and petroleum (b. p. 60–80°) in colourless, six-sided prisms with domed ends. It was analysed in the usual way, by adding an excess of hydriodic acid to a weighed quantity dissolved in chloroform, and estimating the liberated iodine by a standard solution of sodium thiosulphate:—

0.2446 liberated I = 18.7 c.c. N/10 I. Cl as :N:Cl = 13.55.

$C_{14}H_{10}O_2:N$ Cl requires Cl as :N:Cl = 13.65 per cent.

When heated with water or dilute acids it is hydrolysed, hypochlorous acid being liberated and dibenzamide reformed, the latter undergoing further hydrolysis to benzoic acid and benzamide, and finally, if the heating be prolonged, to benzoic acid and ammonia.

Di-*p*-toluyl Nitrogen Chloride, $\begin{array}{c} CH_3 \cdot C_6H_4 \cdot CO \\ CH_3 \cdot C_6H_4 \cdot CO \end{array} > N \cdot Cl$.—

This was prepared from di-*p*-toluylamide by the method previously described. It closely resembles the dibenzoyl derivative in properties and in solubility. It crystallises in long, colourless, six-sided prisms with domed ends (m. p. 129°).

0.2121 liberated I = 14.8 c.c. N/10 I. Cl as :N:Cl = 12.37.

$C_{16}H_{14}O_2:N$ Cl requires Cl as :N:Cl = 12.32 per cent.

The author desires to reserve the further investigation of these and similar compounds.

*112. "The Preparation of Pure Chlorine and its behaviour towards Hydrogen." By J. W. MELLOR and E. J. RUSSELL.

A quantity of carefully dried and purified silver chloride was placed in a V-shaped tube of the hardest Jena glass, in which were also inserted, as electrodes, stout carbon rods specially prepared for the electrolysis of fused salts. An air-tight joint having been made, the salt was fused and a current of 2.8 ampères passed through. Chlorine was evolved in a steady stream. Foreign gases and moisture were removed by occasional reversal of the current, and repeated exhaustion with an automatic Sprengel pump.

The silver tree was destroyed by raising the temperature and increasing the current to 5 ampères. The tree then either melted or was shattered; electrolysis was discontinued until the former temperature was restored; when started again, it was found to proceed in a normal manner.

Hydrogen was prepared by the action of steam on sodium, and was absorbed by palladium. The whole apparatus was then exhausted, the palladium heated, and hydrogen evolved.

The gases were sealed up in the inner and outer bulbs respectively of the condensers now largely used with Soxhlet extractors. Each bulb contained a quantity of carefully purified phosphorus pentoxide, the inner bulb containing also a small piece of glass rod. After drying for some months in the dark, the vessels were shaken to break the inner bulb, and the gases mixed by diffusion. Only condensers which had approximately equal capacities for the inner and outer bulbs were used; hydrogen was put in at the same pressure as the chlorine, so that the volumes of the two gases were nearly equal.

A small electric spark passed through a mixture so obtained caused an explosion, and combination was found to have been practically complete. Apparently drying does not affect the action of the spark.

Mixtures of moist hydrogen and chlorine in similar bulbs were found to explode at about 260°. One of the bulbs containing the purified mixture was therefore heated to 270° for some minutes, but no explosion took place. On opening the bulb, it was found that there had been practically no combination. Another bulb was heated for ten minutes to 450°. Still no explosion occurred, but about 80 per cent of the mixture had combined. Some of the phosphorus pentoxide had volatilised, and as it was found impossible to heat the gases without also heating the pentoxide, it is still uncertain whether this slow combination is a direct action or a surface action. Another bulb was exposed to bright sunshine at Wye for three days, but no explosion took place; and only about 30 per cent of the hydrogen and chlorine had combined.

(To be continued).

A New Reaction for Cholesteroline.—L. A. Tchougaf. —The chlorides of the fatty or aromatic acids when heated with a little cholesteroline in solution in chloroform give characteristic colourations in the presence of $ZnCl_2$. To detect cholesteroline in a practical manner it is best to operate in the following manner:—The cholesteroline is dissolved in anhydrous acetic acid; to the solution we add an excess of chloride of acetyl and a few pieces of chloride of zinc; the colour appears on heating, and attains its maximum intensity after boiling for five minutes over a naked flame; the solution becomes red or rose-coloured according to the amount of cholesteroline present, and it also has a greenish-yellow fluorescent appearance. This reaction is much more sensitive than that of Liebermann, as the colour is still apparent with a dilution of 1 part of cholesteroline in 80,000 parts of liquid.—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 363.

CORRESPONDENCE.

THE PATENT LAW AMENDMENT BILL.

To the Editor of the Chemical News.

SIR,—Among the modifications proposed by Mr. Gerald Balfour to be introduced into his Patent Law Amendment Bill, when he moved the second reading on Friday last, was one the effect of which is probably not generally understood, but which, if adopted, will certainly go far to deprive the Act of practical value, and will most probably render it entirely abortive. I refer to the proposal to remove the jurisdiction in respect of Compulsory Licenses from the High Court and to confer it upon the Judicial Committee of the Privy Council.

The Judicial Committee consists of very eminent lawyers, and commands in consequence a large measure of respect. Its decisions on points of principle would be accepted by the whole community with the utmost confidence; but for the particular subject-matter which it is proposed to refer by this Act to that tribunal, the tribunal is most unsuitable. I will mention only two of its disqualifications.

First, it is the most expensive tribunal in the Kingdom. Costs at the Privy Council are always on the "higher scale"; that is to say, on a scale even higher than what in the High Court is known as the "higher scale" and allowed there only in exceptional cases. As an illustration of the lavish expenditure in costs incidental to proceedings before the Judicial Committee, I may mention that Counsel's fees for a consultation, which in a case before the High Court would amount to three guineas, would, if the same consultation were held in connection with litigation before the Privy Council, amount to ten guineas. These extravagant costs will alone be fatal to the relief proposed by the Bill.

Next, the Judicial Committee has no subordinate judicial staff to whom questions of detail can be referred. In Appeals—and the Judicial Committee was organised to act as an Appellate Court—this does not matter. The Appeal Court decides the point in question and remits the working out of its decision in detail to the lower Court. In this way accounts can be adjusted and all the administrative detail worked out by the machinery of subordinate tribunals organised upon a different plan for the conduct of such business. But when the Judicial Committee is directed to undertake the work of a Court of First Instance this deficiency of a staff of referees becomes a serious defect. It has proved a serious hindrance to the work of the Judicial Committee in other matters of a like kind, and it will certainly cripple the tribunal for the present purpose. It would be absurd to expect the Lords of Appeal to spend hours and days in hearing evidence and argument as to whether a royalty should be at 10 per cent on selling price or 15 per cent on cost price, or, say, a penny a pound. A question of that sort can only be effectually investigated by a referee. Four or five of the most distinguished Judges in the land ought not to be asked to sit in conclave on such a question—and will not do it, whatever the Act of Parliament may say. A Judge of the High Court would not do it; but he would get over the difficulty by sending that part of the enquiry, as he already does the examination of intricate accounts, to an official or a special referee.

These, then, are two of the inconveniences involved in the alteration now proposed; and even if they were all, they would, I submit, be sufficient to justify the strongest possible protest on the part of those interested in the success of our Patent Law against the ill-considered proposal to substitute the Judicial Committee for the High Court as the tribunal to decide on questions of compulsory licenses.—I am, &c.,

J. W. G.

Temple, July 10, 1902.

THE MELTING-POINT OF CHROMIUM.

To the Editor of the Chemical News.

SIR,—With reference to the note by Mr. E. A. Lewis on "The Melting-point of Chromium" (CHEMICAL NEWS, vol. lxxxvi., p. 13), it may be as well to point out that as the specimen he conducted his experiments upon contains 1 per cent of impurities, consisting mostly of aluminium (an element reputed to lower the melting-point of certain metals enormously), it is possible that Mr. Lewis's determination is still faulty as that of the melting-point of the pure metal.

In some careful experiments by Osmond, the melting-point of mild steel (*i.e.*, iron plus at least 0.5 per cent of other matters) was found to be 1475° C., and that of hard steel (iron containing 1.0 per cent other matters) 1410° C. This is a difference of 65° for an addition of 0.5 per cent more of other matters.

As aluminium has probably a very considerable influence upon the melting-point of chromium, it would appear that Mr. Lewis's determination is only of value as a record of the melting-point of the particular alloy used by him, and as such it would be interesting to know the precise nature of the 1 per cent other matters present in it.

Osmond gives the melting-point of a chrome alloy containing 80 per cent of chromium as 1485° C.; this is only 35° below that now found by Mr. Lewis in an alloy containing 19 per cent more chromium. I think it may be fairly implied from the opening sentence of Mr. Lewis's note that it is suggested that the melting-point of pure chromium has now been obtained.—I am, &c.,

T. W. HOGG.

Newburn Steel Works, July 14, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 25, June 23, 1902.

Researches on the Reciprocal Action of two Liquids.—M. Berthelot.—The author examines the action of electric piles formed of two liquids, and finds that currents of measurable intensity are produced. He also finds that there is a development of a true electromotive force capable of attaining a specific and definite limit for each of the systems examined, and which is analogous to Volta's primitive pile. He then determines the intensity of the current produced by such piles, and makes a comparison between the intensity of these and those in which the products of electrolysis are not dissipated by the phenomena of diffusion, polarisation, &c.

Chlorating Properties of a Mixture of Hydrochloric Acid and Oxygen.—Camille Matignon.—Tellurium, gold, and platinum, in all their different forms, are attacked by a mixture of hydrochloric acid and oxygen at temperatures much below that of the oxidation of hydrochloric acid gas in oxygen. This mixture, as can be predicted from theoretical considerations, constitutes a chlorating agent of a great number of materials. In the three cases mentioned, its action can be compared to that of free chlorine.

Acidity of Pyrophosphoric Acid.—H. Giran.—Thomsen determined the heats of neutralisation of a molecule of pyrophosphoric acid successively with one, two, and four molecules of soda. The author now completes the investigation, and to obtain more comparable results he prepares the solid acid and the four anhydrous

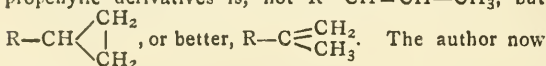
sodium salts. He obtains the following numbers, on the assumption that—

Na sol. + aq. = NaOH diss.	+42.4
P ₂ O ₇ H ₄ sol. + Na sol. = P ₂ O ₇ NaH ₃ sol. . .	+64.8 ⁰
P ₂ O ₇ NaH ₃ sol. + Na sol. = P ₂ O ₇ Na ₂ H ₂ sol. . .	+59.9 ⁶
P ₂ O ₇ Na ₂ H ₂ sol. + Na sol. = P ₂ O ₇ Na ₃ H sol. . .	+46.5 ⁸
P ₂ O ₇ Na ₃ H sol. + Na sol. = P ₂ O ₇ Na ₄ sol. . .	+45.1 ⁸

He therefore finds that pyrophosphoric acid is a tetrabasic acid possessing four strongly acid functions identical with one another.

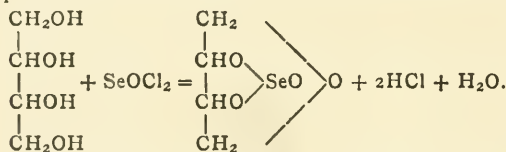
Displacement of Strong Bases by Ammoniacal Cupric Oxide.—M. Bouzat.—The complex base contained in ammoniacal solutions of cupric hydrate is a very strong one. It displaces almost integrally ammonia and its salts. It is nearly as strong as potassium, and in concentrated and strongly ammoniacal solution it precipitates chalk to a very large extent.

Phenylic Migration of Phenylethylene and its Derivatives.—M. Tiffeneau.—M. Bougault showed that the iodohydrines of the derivatives R-CH₂-CH=CH₃ are not decomposed either by HgO or by AgNO₃, whilst iodohydrines of the propenylenic derivatives, R-CH=CH-CH₃, are transformed either by HgO or AgNO₃ into aldehydes, R-CH(CH₃)-CHO; and as, on the other hand, iodohydrine of styrolene gives, under the same conditions, phenylacetic aldehyde, the author concludes that the structure of the initial propenylic derivatives is, not R-CH=CH-CH₃, but



The author now further examines the mechanism of these reactions.

Action of Selenyl Chloride on Erythrite.—C. Chabrière and R. Jacob.—The authors find that the dehydration which erythrite undergoes under the action of selenyl chloride causes it to become a primary alcohol group, and the fixation of selenium takes place in the secondary alcohol groups. The constitution of the product formed, and the reaction causing it, is shown by the following equation:—



Dibenzoylhydrazobenzene.—P. Freundler.—The author repeats the experiments of Biehringer and Busch, and establishes the following reaction:—When benzoic anhydride acts on hydrazobenzene in presence of absolute alcohol at 120° in a sealed vessel, azobenzene is produced, and also a white substance which melts at 161°. This product possesses the properties and composition as described by Biehringer and Busch, but the author finds it to be simply benzanilide.

Acyl Derivatives of Isopyromucic Acid, Acetate, Benzoate, and Pyromucate of Isopyromucyl.—G. Chavanne.—For the purpose of verifying the existence of the phenolic or enolic function of isopyromucic acid, the author examines the action of acid chlorides on this compound. He thus prepares the acetate, benzoate, and pyromucate of isopyromucyl.

MISCELLANEOUS.

Saponification of Nitrate of Ethyl by Water.—E. Biron.—To determine the speed of saponification of nitrate of ethyl by water, the author kept a mixture of water and ether at a constant temperature; the latter must be in excess, so that during the whole of the operation the aqueous solution of the ether remains saturated,

and the concentration is constant; at determined intervals samples of the solution are taken in which the amount of HNO₃ is titrated by means of Ba(OH)₂ in the presence of phthalein. We find that at first the solubility of the nitrate of ethyl in 100 grms. of water (between 55° and 85°) is 2.239-0.03642t+0.0003152t². The experiment shows that the speed of saponification increases in the same ratio as the amount of nitric acid contained in the water, and can be expressed as follows:—

$$\frac{dx}{d\theta} = (k_1 + k_2x)C;$$

x is the amount of ether decomposed, θ the time in hours, C the concentration of the ether, k the constant of the reaction with water, k₂ the constant of catalytic acceleration due to the presence of nitric acid. At the temperature of 70°, C = 0.1481; k = 0.004246; k₂ = 0.0135. We see that the normal nitric acid solution saponifies about 4.17 times quicker than pure water.—*Journ. Soc. Phys. Chim. R.*, vol. xxxii., p. 636.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Extraction of Oil from Seeds.—"Seed Crushing" will find a detailed account of oil crushing in Livache and M'Intosh's "Manufacture of Varnishes, Oil Crushing, Refining, and Boiling" (Scott, Greenwood, and Co.), and also in Andes' "Vegetable Oils" (Second Edition), published by same firm.—J. G. M'INTOSH.

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ST. PAUL'S SCHOOL, West Kensington.—An EXAMINATION will be held at the above School on Tuesday, September 16th, 1902, and the following days, for filling up Twenty or more Vacancies on the Foundation.—Full particulars can be obtained on application to the Bursar.

GUSTAV FOCK, BOOKSELLER, LEIPZIG, wishes to PURCHASE the following Volumes of the *CHEMICAL NEWS*:—I-78, I-8, 19-44, 47-78.

THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2226.

NINTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1901.*

By F. W. CLARKE.

(Concluded from p. 26).

Tellurium.

AN interesting contribution to our knowledge of tellurium is due to Steiner (*Berichte*, xxiv., 570), who has measured its atomic weight by partial analyses of diphenyl telluride. In this compound, by combustion, the carbon was determined, and from that determination the atomic weight of the metal was computed. The data, for two separate fractions of material, are as follows:—

	Weight $C_{13}H_{10}Te$.	Weight CO_2 .	Per cent C.	Atomic weight.
1.	{ 0'2295 0'2559 0'23065	{ 0'5512 0'4811 0'4341	{ 51'39 51'28 51'34	{ 126'1 126'7 126'4
2.	{ 0'2140 0'2578	{ 0'4031 0'4849	{ 51'38 51'31	{ 126'2 126'6
	Mean			126'4

Calculated with $C=12'003$, $H=1'008$. The results are, of course, only approximate, and are intended by the author as an indication of a promising method, and as evidence that the atomic weight of tellurium falls below that of iodine, as demanded by the Periodic Law.

Steiner also gives two analyses of diphenyl selenide, with determinations of the atomic weight of selenium based upon them. The data are:—

Weight $C_{12}H_{10}Se$.	Weight CO_2 .	Per cent C.	Atomic weight.
0'2812	0'6375	61'85	78'8
0'5371	1'2158	61'71	79'3

Another communication upon the atomic weight of tellurium is by Pellini (*Berichte*, xxxiv., 3807), who employed the old methods of oxidation and reduction connecting Te with TeO_2 . His material, however, was purified by means of two organic compounds, diphenyl telluride and diphenyl tellurium dibromide, from which the metal used in the determinations was finally obtained.

First, Te was oxidised to TeO_2 by means of nitric acid. In the first three determinations the dioxide was heated to 400° ; in the remaining four it was fused. The sixth experiment is only partially stated; the figures in the third and fourth columns have been computed by your Committee. The final mean result ($O=16$) is that given by Pellini.

Weight Te.	Weight TeO_2 .	Per cent Te in TeO_2 .	Atomic weight.
1'0679	1'3353	79'968	127'70
1'5469	1'9354	79'926	127'41
2'2386	2'7980	80'007	128'05
2'4522	3'0665	79'967	127'73
2'0977	2'6239	79'945	127'56
2'0442	2'5575	79'929	127'43
2'0434	2'5556	79'957	127'66

Mean 127'65

The reduction experiments, performed in hydrogen by Staudenmayer's method, were only three in number, as follows:—

Weight TeO_2 .	Loss of weight.	Per cent Te in TeO_2 .	Atomic weight.
1'4680	0'2944	79'945	127'56
1'9968	0'3993	80'000	128'02
1'9575	0'3932	79'913	127'30

Mean 127'62

The figures obtained are not remarkably concordant, but they tend to confirm the older determinations, and to place tellurium above iodine.

Still a third memoir upon this atomic weight is due to Koethner (*Liebig's Ann. Chem.*, cccxix., 1), whose work is more than ordinarily elaborate and thorough. His material was scrupulously purified, and studied spectroscopically; and the only (minute) impurities which seem to be possibly present are such as would tend to lower the observed atomic weight. Several methods of determination were attempted, but the final results rest upon the study of the basic tellurium nitrate, $Te_2O_3 \cdot NO_3 \cdot OH$. This salt, on heating under proper precautions, is reduced to TeO_2 . In the second series of determinations, as given below, the tellurium which served as the starting-point had been distilled *in vacuo*; in the first series that precaution was not taken. The weights were not reduced to a vacuum, and the calculations were based upon $O=15'88$, $N=14'93$, and $H=1$.

SERIES I.		
Weight of salt.	Weight TeO_2 .	Atomic weight Te.
2'9373	2'4522	126'39
2'7982	2'3361	126'40
2'8354	2'3840	126'46
Mean		126'41
If $O=16$, Te		=127'36

SERIES II.		
Weight of salt.	Weight TeO_2 .	Atomic weight Te.
5'30270	4'42824	126'67
6'00600	5'01543	126'64
5'58039	4'65990	126'62
28'66904	23'94259	126'73
2'83859	3'20560	126'71
5'85449	4'88930	126'69
25'65029	21'42146	126'70

Mean 126'68
If $O=16$, Te =127'63

These last values are essentially identical with those found by Pellini. The memoir contains criticisms of the recent work of others upon the atomic weight of tellurium, and is unusually complete.

Tungsten.

Taylor (Doctoral Thesis, University of Pennsylvania, 1901), working under the direction of Edgar F. Smith, has made numerous experiments upon the reduction of WO_3 to W, and the reverse oxidation, and has obtained discordant data as to the atomic weight of tungsten. His material was prepared from wolfram, and purified by recrystallisation as ammonium tungstate. The discrepancies are probably to be explained by the presence in the latter salt of small quantities of an ammonium-iron-manganese tungstate. Experiments were also carried out upon the expulsion of CO_2 from Na_2CO_3 during solution in the latter of WO_3 . This work was done somewhat imperfectly, and the results are not of absolute value; they are, however, encouraging, and show that the method has some presumptive merit. The thesis is essentially a study of methods, rather than of actual determinations of atomic weight. It has value, as showing some of the errors which have vitiated former work, and which may now be avoided.

Uranium.

Aloy (*Comptes Rendus*, cxxii., 551; also, more fully, in *Ann. Chim. Phys*, [7], xxiv., 418) has determined the

* *Journal of the American Chemical Society*, vol. xxiv., No. 3.

atomic weight of uranium by a new method, which he proposes to apply to other metals as well. The pure nitrate, of unknown weight, was the material studied. Nitrogen was determined volumetrically, and in the same sample the metal was estimated as UO_2 . From the ratio between these measurements the desired atomic weight was computed. The data given are as follows:—

No.	Volume of N. C.c.	Atomic weight U.
1	15.25	239.3
2	33.5	239.4
3	38.0	239.6
4	52.5	239.5
5	81.25	239.4
6	125.0	239.5
7	151.2	239.4
8	165.0	239.4

The value finally adopted was $U = 239.4$ when $N = 14.04$. The weights of UO_2 obtained are not published in the paper, so that the accuracy of the work cannot well be estimated. Data of this kind, which cannot be re-computed by the reader, are of very little value. It is to be hoped that the paper is only a preliminary statement, and that the full details of the research will appear later.

Lanthanum.

Brauner and Pavlicek (*Proc. Chem. Soc.*, xvii., 63), in determining the atomic weight of lanthanum by synthesis of the sulphate from the oxide, find that the sulphate is always contaminated by Wyrouboff's acid sulphate to a notable extent. The latter salt is so stable that even at 500° some of it remains undecomposed, while another portion of sulphate in the same crucible may have been reduced to a basic compound. Hence all "equivalent" determinations of rare earths hitherto made by the sulphate method are vitiated by this error. Applying, by actual measurement, the necessary correction for excess of acid, and also correcting for the absorption of hygroscopic moisture by lanthanum sulphate, the authors find for the atomic weight of the metal in the most positive fraction of their material, the value $La = 139.0$. Ordinary lanthanum, however, the authors regard as a complex of this true lanthanum with another earth metal.

Praseodymium.

Brauner (*Proc. Chem. Soc.*, xvii., 65) determines the atomic weight of this metal by four methods. First, by analysis of the anhydrous sulphate, whence $Pr = 140.95$. Second, by the analysis of the oxalate, whence $Pr = 140.95$. Third, by synthesis of the sulphate from the oxide, which gave $Pr = 140.78$. Fourth, a series like the third, but with corrections for the presence of acid sulphate and hygroscopic moisture, gave $Pr = 140.93$. The mean result adopted is $Pr = 140.94$. Detailed weighings are not given. An ebullioscopic determination of the molecular weight of praseodymium chloride confirmed the foregoing value.

Neodymium.

Also determined by Brauner (*Proc. Chem. Soc.*, xvii., 66) by means of the sulphate method. Result, corrected for the presence of acid sulphate, $Nd = 143.80$.

Thorium.

By the hydrolysis of thorium oxalate, Brauner (*Proc. Chem. Soc.*, xvii., 68) claims to have decomposed commercial thorina into two earths which he calls Th_α and Th_β . For thorium alpha the atomic weight determinations by the oxalate method gave 233.5, and by the sulphate method 233.3 to 233.7. The most negative fractions of his material, the thorium beta, first gave the value 232.5, which, by further purification was reduced to 232 and 231.9. By continued fractionation an oxide was obtained, giving an atomic weight of $\text{Th}_\beta = 220$. This decrease was accompanied by a reduction in the density of the oxide from 10.2 to 9.6. The complex nature of the

thorium heretofore known may therefore be regarded as proved.

Similar results to those announced by Brauner were independently and almost simultaneously obtained by Baskerville (*Journ. Am. Chem. Soc.*, xxiii., 761). Oxides were prepared, ranging in specific gravity from 8.47 to 11.26, the most definite or real thorium oxide giving values from 9.188 to 9.253. The lowest figures represent an oxide which occurs in small amount in ordinary thorina, the higher to a new earth. The purest thorium compound prepared was a tetrachloride, upon which atomic weight determinations were made, ThO_2 and chlorine being both estimated. Two determinations gave $\text{Th} = 223.2$ and 223.3, or about ten units below the accepted figures. In another sample the value 222.13 was found. To the unknown contamination, which raises the atomic weight of the metal and increases the density of the oxide, an atomic weight of from 260 to 280 must be attributed. This element Baskerville proposes to name carolinium. His paper is confessedly a preliminary communication, and further investigation is in progress. Since his methods of research differ from those of Brauner, the convergence of the results is all the more suggestive.

Older Data.

In Bolton's "Index to Academic Dissertations," published by the Smithsonian Institution, I find the titles of four Russian theses which seem to have escaped the attention of all other writers on atomic weights. Of their value I can say nothing, but as they form part of the literature of the subject I reproduce the titles (as translated in Bolton's work) here:—

Dobrovolsky, V.—"Contributions to the Chemistry of Boron and its Compounds. 1. The Atomic Weight of Boron." Kiev, 1869.

Einbrodt, Paul.—"On the Atomic Weight of Nitrogen." Kharkov, 1840.

Struve, H.—"Dissertation on the Determination of the Atomic Weight of some Elements." St. Petersburg, 1850.

Viluef, V.—"Dissertation on the atomic Weight of Bismuth." St. Petersburg, 1849.

It is to be hoped that some scholar having access to Russian literature may prepare abstracts of these documents, and thereby make the data which are contained in them available for general use.

The Standard of Atomic Weights.

Over this question, controversy still continues. The International Committee of the German Chemical Society publishes its table for 1901 according to both standards; first with $O = 16$, and then in response to a demand from teachers giving a "didactic table" based upon $H = 1$. Both tables are given in this report, at the end. In their third general report (*Berichte*, xxiv., 4358), the same Committee publish many letters from individual chemists, the final outcome from all sources being 106 voices in favour of $H = 1$ and 78 for $O = 16$. This preponderance is offset by the fact that five societies expressed their views as societies, four for $O = 16$, and only one for the hydrogen basis. The Committee, therefore, continues to recommend the oxygen standard. The members of the Verein deutscher Chemiker who protested against the oxygen standard, also publish the results of their canvass among the teachers of chemistry in German-speaking countries (*Zeit. Angew. Chem.*, February 19, 1901), and give the names of the respondents. 104 favoured the hydrogen unit; 19 preferred the oxygen standard. Erdman (*Zeit. Angew. Chem.*, August 20, 1901) has printed a table of atomic weights with $H = 1$, which is in most points identical with that of your Committee, only it is carried out uniformly to two decimal places. The two values in which it varies essentially from ours is in $\text{Co} = 58.80$, or about $\frac{1}{2}$ unit higher, and in $\text{Pd} = 106$ or $\frac{1}{10}$ lower.

In favour of the oxygen standard there is a paper by

Richards (*Zeit. Anorg. Chem.*, xxviii., 355), and the incidental remarks by Sakurai in his essay upon "Some Points in Chemical Education" (read before the Chemical Section of the British Association, 1901, separately printed; see also CHEMICAL NEWS, vol. lxxxiv., p. 151). There is also, on the hydrogen side of the discussion, an elaborate article by Glücksmann (*Zeit. des Allgem. Oesterr. Apotheker-Vereins*, 1901, Nos. 23, 24, 25, 26).

Still another standard of values has been proposed by Hinrichs ("The Absolute Atomic Weights of the Chemical Elements, &c.," published at St. Louis, Mo., 1901), who takes as the experimental basis of his system the atomic weight of "carbon-diamond" as 12 exactly. He seeks to show that all true atomic weights are multiples of the half-unit of hydrogen, but his method of discussion is more polemical than scientific. He reiterates his well-known objections to the work of Stas and the "Stasians," and denounces the conclusions of these men as "false and fraudulent."

Miscellaneous Notes.

Benoist (*Comptes Rendus*, cxxxii., 772), studying the "specific opacity" of substances with regard to the X-rays, finds that for the elements this property is a definite function of the atomic weight. Applying this principle to certain compounds of indium, he shows that the atomic weight of that element must be 113.4 rather than 75.6; that is, the classification of indium as trivalent and not as a dyad is confirmed.

Chabrie and Rengade (*Comptes Rendus*, cxxxii., 472) reach the same conclusion from an ebullioscopic determination of the molecular weight of indium acetylacetonate.

In the report of this Committee for 1900, Demarcay's work on the atomic weight of samarium was cited. He then found the oxide hitherto studied to have been contaminated with another earth of higher atomic weight. Continuing the investigation, he has isolated this earth (*Comptes Rendus*, cxxxii., 1484), which corresponds to a new metal of atomic weight 151. To this metal he gives the name "Europium."

G. and E. Urbain (*Comptes Rendus*, cxxxii., 136), by a prolonged fractionation of the yttria groups, have obtained yttria and ytterbia in a high degree of purity. The atomic weights of the two metals are given, without details, as—

$$Yt = 88.6.$$

$$Yb = 172.6.$$

These values are presumably based upon $O = 16$.

A new earth, resembling and associated with zirconia, has been separated by Hofmann and Prandtl (*Berichte*, xxiv., 1064) from euxenite. They assume that the metal is a tetrad, and determine its atomic weight from two analyses of separate fractions of the sulphate.

Weight of sulphate.	Weight of oxide.	Atomic weight.
0.2176	0.1234	177.6
0.1170	0.0664	177.9

These data are only preliminary, and further investigation is promised.

Strutt (*Phil. Mag.*, [6], i., 311) has applied the calculus of probabilities to the tendency exhibited by atomic weights to approximate whole numbers. No atomic weight can vary from a whole number by more than 0.5. Taking the eight elements Br, C, Cl, H, N, K, Na, and S, and assuming $O = 16$, the sum of the eight deviations from whole numbers is only 0.809. The probability that this sum should not be larger is represented by about one chance in one thousand. Hence the atomic weights tend to approximate the whole numbers to a greater extent than can be accounted for by accident. As Strutt puts the case—"We have stronger reasons for believing in the truth of some modification of Prout's law than in that of many historical events which are universally accepted as unquestionable." A similar discussion, applied to eighteen elements, was once put forth by Mallet, but the mathematical treatment was not the same. There is also a

short paper on the same subject by Rudolphi (*Chemiker Zeitung*, xxv., 1133).

Table of Atomic Weights.

The following table of atomic weights is somewhat differently arranged from that of a year ago. First, your Committee gives its own list, followed by that of the German Chemical Society on the basis of $H = 1$. Then come the three columns, Clarke, Richards, (*Proc. Amer. Acad.*, April, 1901), and the German (accompanying No. 1 of the *Berichte* for 1901, as an extra insertion), on the standard of $O = 16$.

In the light of the foregoing report, some of the values given in the table must be regarded as doubtful. Demarcay's work on samarium, Baskerville's and Brauner's on thorium, and Brauner's upon the other rare earth metals should be taken into account. All of this work, however, needs to be carried further and published more fully before the table should be correspondingly changed. The magnitude of the necessary changes is as yet too uncertain. In the case of thorium, the atomic weight given relates to that mixture of earths which has hitherto been called thorina, and which we actually meet in analytical operations.

	$H = 1.$		$O = 16.$		
	Clarke.	German.	Clarke.	Richards.	German.
Aluminum ..	26.9	26.9	27.1	27.1	27.1
Antimony ..	119.5	119.1	120.4	120.0	120.
Argon ..	39.6	39.6	39.96	39.92	39.9
Arsenic ..	74.45	74.4	75.0	75.0	75.
Barium ..	136.4	136.4	137.40	137.43	137.4
Bismuth ..	206.5	206.9	208.1	208.	208.5
Boron ..	10.9	10.9	11.0	11.0	11.
Bromine ..	79.35	79.36	79.95	79.955	79.96
Cadmium ..	111.55	111.6	112.4	112.3	112.4
Cæsium ..	131.9	132.	132.9	132.9	133.
Calcium ..	39.8	39.7	40.1	40.1	40.
Carbon ..	11.9	11.91	12.0	12.001	12.00
Cerium ..	138.0	139.	139.0	140.	140.
Chlorine ..	35.18	35.18	35.45	35.455	35.45
Chromium ..	51.7	51.7	52.1	52.14	52.1
Cobalt ..	58.55	58.56	59.00	59.00	59.
Columbium ..	93.0	93.3	93.7	94.	94.
Copper ..	63.1	63.1	63.60	63.60	63.6
Erbium ..	164.7	164.8	166.0	166.	166.
Fluorine ..	18.9	18.9	19.05	19.05	19.
Gadolinium ..	155.2	155.	156.4	156.?	156.
Gallium ..	69.5	69.5	70.0	70.0	70.
Germanium ..	71.9	71.5	72.5	72.5	72.
Glucinum ..	9.0	9.03	9.1	9.1	9.1
Gold ..	195.7	195.7	197.2	197.3	197.2
Helium ..	3.93	4.0	3.96	3.96	4.
Hydrogen ..	1.000	1.00	1.008	1.0075	1.01
Indium ..	113.1	113.1	114.0	114.	114.
Iodine ..	125.89	125.90	126.85	126.85	126.85
Iridium ..	191.7	191.5	193.1	193.0	193.
Iron ..	55.5	55.6	55.9	55.9	56.
Krypton ..	81.15	81.2	81.76	81.7	81.8
Lanthanum ..	137.6	137.	138.6	138.5	138.
Lead ..	205.36	205.35	206.92	206.92	206.9
Lithium ..	6.97	6.98	7.03	7.03	7.03
Magnesium ..	24.1	24.18	24.3	24.36	24.36
Manganese ..	54.6	54.6	55.0	55.02	55.
Mercury ..	198.50	198.8	200.0	200.0	200.3
Molybdenum ..	95.3	95.3	96.0	96.0	96.
Neodymium ..	142.5	142.5	143.6	143.6	143.6
Neon ..	19.8	19.9	19.94	19.94	20.
Nickel ..	58.25	58.3	58.70	58.70	58.7
Nitrogen ..	13.93	13.93	14.04	14.04	14.04
Osmium ..	189.6	189.6	191.0	190.8	191.
Oxygen ..	15.88	15.88	16.000	16.000	16.00
Palladium ..	106.2	105.2	107.0	106.5	106.
Phosphorus ..	30.75	30.77	31.0	31.0	31.0
Platinum ..	193.4	193.3	194.9	195.2	194.8
Potassium ..	38.82	38.86	39.11	39.14	39.15

	H = 1.		O = 16.		
	Clarke.	German.	Clarke.	Richards.	German.
Praseodymium ..	139.4	139.4	140.5	140.5	140.5
Rhodium ..	102.2	102.2	103.0	103.0	103.0
Rubidium ..	84.75	84.76	85.4	85.44	85.4
Ruthenium ..	100.9	100.9	101.7	101.7	101.7
Samarium ..	149.2?	148.9	150.3?	150.	150.
Scandium ..	43.8	43.8	44.1	44.	44.1
Selenium ..	78.6	78.5	79.2	79.2	79.1
Silicon ..	28.2	28.2	28.4	28.4	28.4
Silver ..	107.11	107.12	107.92	107.93	107.93
Sodium ..	22.88	22.88	23.05	23.05	23.05
Strontium ..	86.95	86.94	87.60	87.68	87.6
Sulphur ..	31.83	31.83	32.07	32.065	32.06
Tantalum ..	181.5	181.6	182.8	183.	183.
Tellurium ..	126.1	126.	127.7	127.5?	127.
Terbium ..	158.8	—	160.	160.	—
Thallium ..	202.61	202.6	204.15	204.15	204.1
Thorium ..	230.8?	230.8	232.6?	233.	232.5
Thulium ..	169.4	170.	170.7	171.?	171.
Tin ..	118.1	117.6	119.0	119.0	118.5
Titanium ..	47.8	47.7	48.15	48.17	48.1
Tungsten ..	182.6	182.6	184.	184.	184.
Uranium ..	237.8	237.7	239.6	238.5	239.5
Vanadium ..	51.0	50.8	51.4	51.4	51.2
Xenon ..	127.	127.	128.0	128.	128.
Ytterbium ..	171.9	172.	173.2	173.	173.
Yttrium ..	88.3	88.3	89.0	89.0	89.
Zinc ..	64.9	64.9	65.4	65.40	65.4
Zirconium ..	89.7	90.0	90.4	90.6	90.7

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, July 8th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us chemically during the month, all were found to be clear, bright, and well filtered.

Although there has been a considerable excess of rain in London during the past month, viz., 1.66 inches or 86.0 per cent, the same cannot be said for Oxford, which place we have always taken as being about the centre of the Thames watershed; it must also be remembered that no rain that falls below Ilampton, where the intakes are, affects the London water supply derived from the Thames. The actual rainfall recorded at Oxford during June was

only 1.96 inches, the average fall is 2.10 inches, making a deficit of 0.14 inch, which, added to the previous one, makes a total deficit for the first six months of the year of 3.30 inches, or 30.5 per cent on the thirty-five years' average.

Our bacteriological examinations of 509 samples have given the results recorded in the following table; we have also examined 41 other samples, from special standpipes, wells, &c., making a total of 550 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 25 samples) ..	312
New River, filtered (mean of 129 samples) ..	16
Thames, unfiltered (mean of 25 samples) ..	4338
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 272 samples) ..	32
Ditto ditto highest	538
Ditto ditto lowest	0
River Lea, unfiltered (mean of 25 samples) ..	464
River Lea, from the East London Company's clear-water wells (mean of 33 samples) ..	35

Of the 434 samples taken daily from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, fifteen samples, or 3.4 per cent, were sterile. Thirteen samples contained more than 150 microbes, while twenty-five samples, or 5.7 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the twenty-five excess samples was 206, against a corresponding mean of 173 in thirty excess samples during May. This increase was caused by the sudden rainfall at the beginning of the month, when the microbic impurity in the raw Thames Water rose very considerably, thereby throwing extra strain on the filters. Special bacteriological examinations have revealed the presence of none but harmless river microbes.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

ACTION OF BROMINE ON THALLOUS CHLORIDE IN THE PRESENCE OF ORGANIC SOLVENTS, AND BY THE DRY METHOD.

By V. THOMAS.

As has been pointed out in previous papers, we cannot easily obtain the intermediate chlorobromides, regularly formed by the addition of bromine to thallous chloride, when working in contact with water. As we have said, the cause of this want of success can be found in the dissolving action of water on the intermediate compounds at first formed.

In the hope of succeeding in the preparation of the chlorobromides, we decided to use as solvents organic compounds such as chloroform, sulphide of carbon, and tetrachloride of carbon. In the presence of these solvents the bromination is immediately shown to be different from the bromination in the presence of water, inasmuch as the fixation of the bromine stops when we reach the type Tl_2X_4 .

A point not less interesting to note is the non-formation of normal compounds of addition. As, when we operate in the presence of water, chlorobromides are always formed less rich in chlorine than the product with which we start; that is to say, containing less than one atom of chlorine for one atom of thallium. It is probable that here again we may admit the transitory formation of normal compounds of addition, of thallosothallic chlorobromide, for example.

These in the presence of solvents do not undergo any dissociation, as when in contact with water, into thallic compounds or compounds containing less of the halogen,

but they enter into reaction with the solvent itself in a more or less complex manner.

I. *Action of Bromine on TlCl in the presence of Chloroform.*—4.8 grms. of thallous chloride, 2.8 grms. of bromine, and 40 grms. of the solvent were left for a long time in a ground stoppered flask. The thallous chloride takes a yellow tint, which at first increases in intensity and then seems to become slightly paler.

Analysis.—Found, AgCl+AgBr, 104.31, and 104.02; Cl, 6.76 and 7.80; Br, 30.67 and 30.98. Calculated for $Tl_2Cl_2Br_4$:—AgCl+AgBr, 103.58; Cl, 7.08; Br, 31.90.

As will be seen, the analysis shows a slight excess of chlorine; the cause for this will be found in the difficulty experienced in effecting the transformation in a complete manner.

If we evaporate the solution from which the yellow powder has been separated, we obtain fine yellow needles of the same composition.

II. *Action of Bromine on TlCl in the presence of Sulphide of Carbon.*—Sulphide of carbon is a very bad solvent in which to effect the bromination of thallous chloride. The reaction is very complex.

We might suppose that two phenomena are produced at the same time; on the one hand, the bromination of thallous chloride and the setting free of the chlorine, and on the other hand, the action of the halogens on the sulphide of carbon.

The part played by the solvent can be demonstrated in a very simple manner; it is sufficient to leave a small quantity of chloride of thallium, sulphide of carbon, and bromine in a test-tube for several days. Fumes having the very characteristic odours of halogen compounds of sulphur are given off. After a sufficient time, especially if we use a sufficient quantity of bromine, the tube commences to show long needles. These needles do not contain thallium, but apparently represent compounds analogous to those mentioned by Hell and Urech (*Ber.*, vol. xv., p. 909; and vol. xvi., p. 1144), for which these chemists proposed the formulæ CS_2Br_4 , $C_2Br_6S_3$, $C_6Br_4S_4+2H_2O$.

It is certain that in such a reaction the thallous chloride is principally a "carrier" for the halogen; that is an action that has long been well known. In trying to discover what becomes of the thallous salt originally added in this reaction, we readily observe that it is not confined to assisting the halogenation of the sulphide of carbon. It itself comes into play, and is found in the products of the reaction in the form of the dibromide, $TlBr_2$, more or less impure.

By adopting suitable conditions we can obtain a yellow product containing:—Found, Cl, 0.23; Br, 43.31. Calculated, Cl, 0.00; Br, 43.9.

In this reaction the thallous chloride is susceptible of completely exchanging its chlorine for bromine. Thus it resembles ferric chloride, which, as we have shown, is able, even in the aromatic series, to effect the substitution of the chlorine for bromine or iodine (*Comptes Rendus*, July 18, 1898).

III. *Action of Bromine on TlCl in the presence of Tetrachloride of Carbon.*—Here the same phenomena are observed as when employing chloroform for the solvent. The analyses all show a considerable excess of bromine and a deficit of chlorine. Found, Br, 33.97 and 33.50; Cl, 6.13 and 6.33. Calculated for $Tl_3Cl_2Br_4$:—Br, 31.90; Cl, 7.08.

Possibly in effecting the bromination under special conditions, with heat for instance, we might succeed in replacing the whole of the chlorine by bromine.

However this may be, if we use an impure tetrachloride containing sulphide of carbon even in very small quantities, we immediately notice the presence of the halo-derivative of sulphur; at the same time almost complete bromination takes place. In this manner we have obtained a product corresponding to the following composition:—Found, Br, 43.10; Cl, 0.28. Calculated for $TlBr_2$:—Br, 43.90; Cl 0.00.

IV. *Action of Bromine on Thallous Chloride by the Dry Method.*—When, instead of operating in the presence of a solvent, we use the dry method, it is easy to show that:—(1) Normal compounds of addition are formed; (2) the ultimate term of bromination corresponds, under ordinary conditions, to the type $TlClBr$.

This chlorobromide is the one constantly obtained either with bromine and the chloride in the cold, or at a higher temperature, in sealed tubes for instance.

The only really practicable method for preparing this body consists in heating the materials in sealed tubes at 100–125°. In this manner we obtain a product which on analysis gives the following figures:—Found, Br, 25.50 and 24.86; Cl, 11.06 and 10.61. Calculated for $TlClBr$:—Br, 25.03; Cl, 11.11.

This compound shares the properties of both the corresponding chloride and bromide. It is of a deeper yellow than the chloride. Like this salt, its colour rapidly becomes darker on heating and regains its original tint on cooling. Water decomposes it rapidly with the formation of a chlorobromide of the type Tl_4X_6 .—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 11.

EXPERIMENTAL RESEARCHES ON THE CONSTITUTION OF CRYSTALS.*

By A. E. TUTTON, B.Sc., F.R.S., F.C.S.

(Continued from p. 32).

IN turning now to the consideration of the optical characters of the crystals of the series of salts in question, it will be necessary to remember two main facts. The first is, that the symmetry of the rhombic system, in which the sulphates and selenates of the alkalis crystallise, determines that the velocity of light transmission shall be different along the three morphological axes of the crystals, and that two of these directions shall be those of maximum and minimum velocity respectively. In other words, the ellipsoid which, as is well known, in general represents the velocity of light transmitted through a crystalline medium, is one whose three rectangular axes are of unequal lengths, but which is fixed in direction, for these axes are identical in direction with the three morphological axes. The second is, that in the case of the monoclinic double sulphates and selenates the symmetry of the system demands that only one of the three rectangular axes of the optical ellipsoid shall be identical with a morphological axis, the latter being the one symmetry axis of the system. The ellipsoid may therefore be regarded as free to rotate about this axis, for the inclination of the other two rectangular axes of the ellipsoid, which lie in the plane of symmetry, may be any whatsoever with respect to the two inclined morphological axes which lie in that plane.

Within the three models of sections of our rhombic sulphate crystals you now see three illuminated ellipses. They represent the sections of the three optical ellipsoids; but in this case the inner one corresponds to the caesium salt, and represents the ellipsoidal line to which light waves emanating from the imaginary centre of the crystal would penetrate in a given interval of time. The middle one shows the distance to which they would penetrate if the crystal were one of rubidium sulphate or selenate; and any point on the outer one, which is much nearer to the middle one than the outer one is, represents the position at which the light waves would arrive in the same interval of time if the crystal were one of potassium sulphate or selenate.

The velocity with which light travels through the crystals of the three salts is thus observed to vary in the same manner as does the atomic weight of the alkali metal present in the salt.

* A Lecture delivered at the Royal Institution of Great Britain, Friday, May 2, 1902.

In the case of the monoclinic double sulphates and selenates, we have a further phenomenon of even greater interest exhibited. For not only does the velocity along the three rectangular axes of the ellipsoid vary with the atomic weight, but the possible rotation of the whole ellipsoid about the symmetry axis is found to actually occur; and to occur, moreover, to a very considerable extent, sometimes amounting to as much as 20°.

Further, most interesting of all, the rotation varies in a perfectly regular manner throughout all the triplets, in accordance with the atomic weight of the alkali metal present in the salt. This may be demonstrated to you by means of the lantern slide which you now see projected on the screen. You observe the outline of a crystal, arranged so that the screen represents the symmetry plane, and within it an ellipsoid. The latter is at present arranged as it is usually situated in any potassium salt of the series, its major axis being inclined so that its top is somewhat to the left of the vertical morphological axis. The ellipsoid will now be rotated to the approximate position, further on the left of the vertical axis, which it occupies in any rubidium salt of the series, by means of a simple mechanical device; and again it is rotated much further, to about the situation which it takes up in any caesium salt.

In this phenomenon the accelerating progression according to the atomic weight of the alkali metal is beautifully exhibited.

It may now interest you to learn how these results have been obtained. We have to determine, first the position of the optical ellipsoid, and next its dimensions. That is to say, we have to determine the velocity of light transmission in all the various directions in the crystal. Determinations of the refractive index in different directions will afford us the necessary data, and if we can discover the directions of maximum and minimum velocity we shall obtain all that we require if we make the determinations of refractive index for these two directions, and for a third direction at right angles to the plane containing them. For these three directions will be those of the three axes of the ellipsoid.

It will be next demonstrated to you how we discover the positions of the axes of the optical ellipsoid.

It is scarcely necessary to introduce to a Royal Institution audience the magnificent pair of Nicol prisms which formerly belonged to the late Mr. Spottiswoode. The analysing Nicol is at present arranged with its vibrating direction parallel to that of the polarising prism, and to the horizontal cross-wire which you see appearing on the screen, so that light passes to the screen.

There is also focussed the outline of a section of a monoclinic crystal, placed between the two Nicols, and which you may take as representing a crystal of one of our double sulphates or selenates; for it behaves precisely similarly, and is immensely larger than any crystal that could be obtained of one of those salts. We now rotate the analyser so that its vibrating direction is at right angles to that of the polariser, when you see the crystal section brilliantly coloured on the dark field.

If, however, we rotate the crystal section in its own plane, you observe that the coloured light becomes weaker, until, at a certain position, it is altogether extinguished. Further rotation causes light to again appear, and if we complete the circle of rotation we shall find that the crystal becomes four times dark and four times light. That is, there are two directions, at right angles to each other, in which extinction occurs. These two directions are those of two axes of the optical ellipsoid. If the crystal is so prepared as to show on its edge traces of one or two natural faces, and if our rotating stage is divided, it is quite easy to determine the angle between any given trace of a face and either of the extinction directions. In the case of monoclinic crystals the section is cut parallel to the symmetry plane, and the reference edge will usually be a trace of one of the faces in the primary zone perpendicular to the symmetry plane. That

is the case with the two faces whose traces you see are left after the grinding of the large section you observe on the screen. A much more refined method of measuring the angle between the extinction direction and the basal plane based on this principle, was employed in the research.

We will next illustrate the determination of the three refractive indices, corresponding to the three velocities along the three axes of the ellipsoid. There is here a large 60°-prism of a crystal which behaves similarly to the salts we are discussing, and which has been specially cut and polished for this lecture by Mr. Hilger. The refracting edge is parallel to an axis of the ellipsoid. Employing it in the usual manner to throw a spectrum on the screen, we observe that instead of a single spectrum, as when we use a prism of glass, we have two spectra produced, differing considerably in their dispersion. Moreover, on placing a Nicol prism in the path of the light, we see that these spectra consist of polarised light, for one extinguishes when the Nicol is arranged with its vibration direction at 0°, and the other when the Nicol is at 90°. One of the spectra, in fact, is formed by light vibrating parallel to the refracting edge, and therefore to that axis of the ellipsoid which runs parallel with it, and the other by light vibrating at right angles to that direction. If, in cutting our prism, we make this perpendicular direction to coincide with a second axis of the ellipsoid, the two spectra, when set to their minimum deviation, will, provided we know also the angle of the prism, at once afford us the data for computing the refractive indices corresponding to the two axes of the ellipsoid in question. A second prism, similarly cut so as to have vibration directions parallel to one of these axes and to the third axis, will afford us the third refractive index as well as a repetition of one of the first two.

You observed that the two spectra are considerably separated on the screen. If the two axial directions are those of maximum and minimum velocity, the amount of separation is a measure of the double refraction. Now it has been observed that the amount of the double refraction also varies progressively according to the atomic weight, and this fact may be illustrated realistically by means of a carefully made lantern-slide, reproducing the actual positions, as seen in the spectrometer, of the two spectra afforded by a triplet of salts. The triplet chosen consists of potassium zinc sulphate, rubidium zinc sulphate, and caesium zinc sulphate. The spectra are represented by the images of the spectrometer slit for two wave-lengths of light, those corresponding to the red and greenish-blue hydrogen lines. The spectra were produced by three prisms of the respective salts, of precisely the same angle, near 60°. You see that the two upper spectra, representing the potassium salt, are the furthest apart, and that the separation diminishes for the rubidium salt, and it becomes so much less in the case of the caesium salt that the two lower spectra formed by this salt partially overlap.

This relative behaviour as regards double refraction is quite general throughout all the four series of salts.

The point can be further illustrated by the curves which you now see projected on the screen. The two outer curves represent the maximum and minimum refraction, and the inner one the intermediate refraction along the third rectangular axis of the ellipsoid. You observe that the two outer curves converge towards each other as the atomic weight of the alkali metal increases.

This leads in four particular cases to perhaps the most interesting of all the results derived from the work. We will illustrate it by the case of caesium magnesium selenate. The curves which you now see on the screen are those for the magnesium triplet of double selenates. On arrival at the caesium salt the convergence has actually brought the curve for the minimum refraction into contact with that for the intermediate refraction, so that we have here a crystal whose total double refraction is exceptionally small, and in which the velocities along

two of the three ellipsoidal axes are approximately equal, which is characteristic of tetragonal or hexagonal crystals, but a perfect anomaly in a monoclinic crystal. Let us see, however, if the identity is a fact for all wave-lengths, as would be the case in a truly uniaxial crystal of tetragonal or hexagonal symmetry. We will reproduce for you the appearance in the spectrometer afforded by a prism so cut as to give us the two spectra corresponding to these two intersecting curves; that is, whose vibration directions are those of the two apparently equal axes of the velocity ellipsoid.

The images in three colours which you see are those corresponding to the wave-lengths of red lithium light, green thallium light, and violet hydrogen light. You observe that they completely overlap, and if we only used the same magnification as we used for the other images we saw just now, you would say that they are absolutely identical images. We are attempting to faithfully reproduce the whole phenomena by the use of separate slides, shown by two equal lanterns, and when one of them is shut off, the effect is exactly as when a Nicol is introduced at 0° in the spectrometer, which extinguishes one of the spectra. When the other is shut off instead, what you observe is the same as if we rotated the Nicol to 90° , which would extinguish the second spectrum. Commencing with both lanterns on, as when no Nicol is being used, or if it is, it is arranged at 45° , and examining the images closely, we notice that the red and violet images are distinctly double, while the central green image is a truly single one. Now we cut off one lantern, and you please imagine that we are introducing a Nicol at 0° ; the effect has been that the outermost image in the case of both red and violet has disappeared. Now shutting off the other lantern instead, and you please imagine we are rotating the Nicol to 90° , the innermost images disappear. All this time the green image remains fixed and single. This evidently means that for the middle part of the spectrum there is absolute identity of refraction and therefore of velocity, while for the red end there is a minute difference of refraction in one sense, and for the violet end a similar small difference in the opposite sense. The fact is, the two images, corresponding to the two ellipsoidal axes, for red are slightly separated; they approach and coalesce for green; then they pass each other and re-separate on the opposite side of each other as violet is approached.

Thus our crystal is only truly uniaxial for one wave-length of light, and this apparent anomalous refraction is merely the effect of the operation of the rule of progression.

You will have gathered that for the prosecution of this work it has been necessary to prepare some hundreds of 60° -prisms and parallel-sided section-plates, all accurately cut to the desired orientation with respect to the crystal faces. For this purpose it has been found necessary to have the delicate apparatus constructed which you see before you on the table, and a photograph of which is also thrown on the screen. The crystal held in a grip-holder, is suspended from a refined apparatus which serves not only for the adjustment of a zone of the crystal's faces to the vertical axis of the instrument, as determined by the observer through the telescope of the collimator signal-slit, but also, as the movements are graduated, for its setting to any position with respect to the axis. Separate and interchangeable cutting and grinding gear are provided, and also a delicate means of varying the pressure of the crystal on the grinding disc, so that the most fragile crystals can be manipulated without danger of fracturing them.

It is not too much to say of this instrument, that without it the work described to you this evening would never have been possible.

Another original instrument which you see before you is an apparatus for producing spectrum monochromatic light of any wave-length whatsoever. For all the optical researches have to be carried out in pure monochromatic light; that is, for a series of colours of light, each of

which is composed of vibrations of as nearly one wave-length as possible; for all the optical constants vary considerably for different wave-lengths of light. It is essentially a spectroscopic constructed to transmit as large a proportion of the light as possible which streams from the condenser of an electric lantern; a broad spectrum is produced by a highly refractive prism, and is focussed on the back of a second slit, which permits only a selected line of the spectrum to escape, in the same manner as in the well-known apparatus of Sir Wm. Abney. By rotation of the prism the spectrum is moved over the exit slit, so as to permit any desired colour to escape, whose wave-length is known from the reading of the calibrated circle on which the prism is mounted.

The apparatus is placed before you just as it is arranged, in front of the goniometer-spectrometer, when determining refractive indices for a series of different wave-lengths.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, June 18th, 1902.

Prof. EMERSON REYNOLDS, Sc.D., V.P.R.S., President, in the Chair.

(Concluded from p. 34).

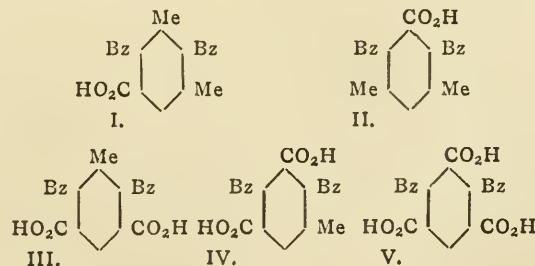
*113. "Derivatives of Dibenzoylmesitylene." By W. H. MILLS and T. H. EASTERFIELD.

The authors described a method of preparing dibenzoylmesitylene by which it may be obtained in quantity, and methods for the production and isolation of the five acids which result by the successive oxidation of its methyl groups, namely, *asym.*dibenzoylmesitylenic acid, m. p. 174° , *sym.*dibenzoylmesitylenic acid, m. p. 222° , *asym.*-dibenzoylulvic acid, m. p. 211° , *sym.*dibenzoylulvic acid, m. p. 262° , and dibenzoyltrimesic acid, m. p. 250° .

A mixture of these, of which *asym.*dibenzoylmesitylenic acid is by far the largest constituent, is obtained by boiling the ketone with dilute nitric acid the boiling-point of which has been raised by the addition of large quantities of potassium and sodium nitrates.

The two dibenzoylulvic acids are most conveniently prepared by treating the easily obtainable *asym.*dibenzoylmesitylenic acid with one equivalent of potassium permanganate in alkaline solution. If double this amount of potassium permanganate be used, dibenzoyltrimesic acid is obtained.

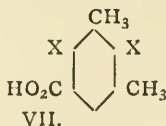
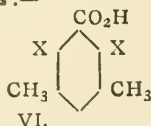
The constitution of these acids readily follows from the following facts:—



The dibenzoylmesitylenic acid of melting-point 174° , oxidised with potassium permanganate, yields a mixture of *both* dibenzoylulvic acids. It must therefore be the asymmetrical acid of formula I. The dibenzoylmesitylenic acid of melting-point 222° , similarly treated, yields only one dibenzoylulvic acid melting at 211° . Hence, it must

be represented by formula II., and the dibenzoylglutic acid resulting from it by IV. The dibenzoylglutic acid melting at 262° must therefore be represented by III., and for dibenzoyltrimesic acid only one formula is possible, namely, V.

In working with these acids, the fact was discovered (also noticed by Graebe, *Ber.*, 1900, xxxiii., 2026) that diortho-substituted acids do not obey V. Meyer's esterification rule when the ortho-substituents are benzoyl groups:—

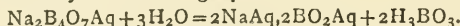


whereas it follows from V. Meyer's work that the esterification constant of an acid of formula VI. would in general be indefinitely smaller at the ordinary temperature than that of an acid of formula VII., in the case where X is a benzoyl group it is smaller only in the ratio of approximately 0.65 to 1.0.

114. "The Molecular Condition of Borax in Solution." By H. S. SHELTON.

Borax (Shields, *Phil. Mag.*, 1893, xxxv., 365) is slightly hydrolysed into sodium hydroxide and boracic acid. Experiments on the diminution of conductivity on the addition of further quantities of boracic acid show an increase of this hydrolysis when further diluted with water, and also with increase of temperature. In N/10 solution, the hydrolysis was estimated by Shields to be 0.5 per cent at 25° , and the experiments of the author with N/200 solution showed 4 per cent at 25° , and 6 per cent at 50° . Kahlenberg and Schreiner (*Zeit. Phys. Chem.*, 1896, xx., 547) concluded from freezing-point determinations that six chemical individuals are present in a dilute solution of borax.

These chemical individuals seem to be $2\text{H}_3\text{BO}_3, 2\text{NaBO}_2$, as shown by the following equation:—



The author has confirmed this by a number of direct experiments, amongst which the most important is the precipitation of AgBO_2 , and determination of the boracic acid remaining in the solution.

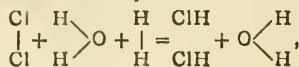
115. "On the Union of Hydrogen and Chlorine." Part V. By J. W. MELLOR, D.Sc.

There is no experimental evidence to show that chlorine gas under the influence of light undergoes any change capable of appreciably affecting the chemical activity of that element towards hydrogen. Part of the energy absorbed by moist chlorine from sunlight is dissipated as heat. This causes the Budde effect. Under the influence of light, chlorine sets up and maintains in a state of equilibrium a reversible reaction with water vapour, possibly $2\text{H}_2\text{O} + 2\text{Cl}_2 \rightleftharpoons 4\text{HCl} + \text{O}_2$. Dry chlorine does not exhibit the Budde effect. The rise in temperature of imperfectly dried chlorine when exposed to sunlight appears to be due to some chemical reaction between the moisture and the chlorine gas. A layer of moist chlorine just thick enough to screen a bulb of mixed hydrogen and chlorine gases from chemical action is not sufficient to prevent chemical action if the chlorine is dried by means of purified phosphorus pentoxide. The actinic energy continuously absorbed from sunlight by moist chlorine is dissipated in at least three ways:—(1) In maintaining the above chemical reaction; (2) by conversion into heat during molecular impacts; (3) as external non-actinic radiations from the molecules moving in their free path between molecular collisions.

116. "On the Union of Hydrogen and Chlorine." Part VI. By J. W. MELLOR, D.Sc.

If the reaction between hydrogen and chlorine in the presence of moisture is assumed to take place with the

formation of an intermediate compound, the period of induction is a direct consequence of the law of mass action. Since neither chlorine monoxide nor hydrogen hypochlorite abbreviate the period of induction, neither of these substances can take part as intermediate compounds in the reaction between hydrogen and chlorine. Since chlorine acquires no appreciable chemical activity by exposure to sunlight, the presence of hydrogen as well as of moisture determines the greater chemical activity of an induced mixture of hydrogen and chlorine gases. If an intermediate compound takes part in the reaction between hydrogen and chlorine in the presence of moisture, the most probable "compound" satisfying the required conditions contains $x\text{Cl}_2, y\text{H}_2\text{O}, z\text{H}_2$, where x, y, z are positive integers. The explanation offered by the two dependent reactions involved in the equation,—



remains to be studied.

117. "On some Hydroxy-pyrone Derivatives." By T. TICKLE and J. N. COLLIE, F.R.S.

During some work on the constitution of meconic acid, the authors found that it was necessary to prepare certain hydroxypyrone derivatives in order to compare their properties (especially their colour reactions with ferric chloride) with those of meconic acid.

Dimethylpyrone, when treated with hydrogen peroxide in presence of a ferrous salt, yields hydroxydimethylpyrone, $\text{C}_7\text{H}_8\text{O}_2 + \text{H}_2\text{O}_2 = \text{C}_7\text{H}_8\text{O}_3 + \text{H}_2\text{O}$. This substance crystallises from water in colourless needles; it can be sublimed without decomposition, and melts at 162.5° . With ferric chloride it gives a deep violet-blue colour. Its monacetyl derivative melts at 98° , and does not colour an aqueous solution of ferric chloride.

Meconic acid, when treated in the same manner with hydrogen peroxide, gives carbon dioxide and hydroxycomeconic acid, $\text{C}_7\text{H}_4\text{O}_7 + \text{H}_2\text{O}_2 = \text{C}_6\text{H}_4\text{O}_6 + \text{CO}_2 + \text{H}_2\text{O}$. Hydroxycomeconic acid seems to be a dibasic acid; it gives an intense violet with ferric chloride, melts at 275° , and crystallises from water in long, fine needles. It seems probable that this is the same acid as that first obtained by Reibstein (*Journ. Pr. Chem.*, 1881, [2], xxiv., 286) by the action of barium hydroxide on bromocomeconic acid. He, however, gives no melting-point for the acid, but only for the ethyl ester, 204° , and for the diacetoxy derivative, 75° . The authors find that these derivatives prepared from this acid melt at 207.5° and 75° respectively.

All attempts to prepare either meconic acid or hydroxycomeconic acid by oxidation of chelidonic acid were unsuccessful.

118. "The Absorption Spectra of Phloroglucinol and some of its Derivatives." By W. N. HARTLEY, D.Sc., F.R.S., J. J. DOBBIE, D.Sc., M.A., and A. LAUDER, B.Sc.

Phloroglucinol reacts with some reagents as a phenol, with others as a ketone. It is impossible, therefore, from its chemical behaviour to decide whether its oxygen atoms are present in hydroxyl groups or in direct union with carbon. The trimethyl derivative of phloroglucinol (m. p. 52°) is regarded as a true ester, since its methoxy groups are split off by heating with hydrogen iodide. The absorption spectra of this substance and of phloroglucinol were found to be almost identical. From this it follows that if the structure of the ester has been correctly established, phloroglucinol also must have the enolic structure (*Trans.*, 1899, lxxvi., 640; 1900, lxxvii., 839). Aqueous and alcoholic solutions of phloroglucinol show both general and selective absorption. A layer 50 m.m. thick of a solution containing 1 milligram.-mol. in 20 c.c. water absorbs all rays beyond λ 3009, whilst a layer 5 m.m. thick absorbs all rays beyond λ 2802. The absorption-band is not strongly marked; it appears first in a layer 3 m.m. thick of the solution containing 1 milligram.-mol. in 100 c.c. water, and nearly dies out in a layer 2 m.m. thick, al-

though its position is still distinctly traceable by the weakness of the spectra in solutions of greater dilution. The resemblance between the spectra of phloroglucinol and the trimethyl derivative is so close that phloroglucinol cannot consist of a mixture of the enolic and ketonic forms.

The specimens of phloroglucinol examined were prepared from five different sources, namely, kino, maclurin, resorcinol, phenol (by fusion with sodium hydroxide), and phloroglucinoltricarboxylic ester. The specimens from these various sources had the same melting-point. The melting-point is greatly influenced by the rate of heating, varying between 210° and 217° . The absorption curves of all the specimens agree perfectly. The authors conclude from the identity of the spectra that the structure of phloroglucinol, no matter from what source it is obtained or by what method it is prepared, is always the same.

The spectra of pyrogallol were also re-examined, and the curve was found to resemble very closely that of phloroglucinol, thus confirming the conclusion that the latter substance has the enolic structure.

119. "Solubility of Mannitol, Picric Acid, and Anthracene." By A. FINDLAY.

Determinations of the solubility of mannitol in water, of picric acid in water and in benzene, and of anthracene in benzene, have been made at several temperatures between 25° and 60° .

It has already been shown by the author (*Proc. Roy. Soc.*, 1902, lxi., 471) that if the solubility curve of one substance is known, that of another substance can be calculated from two, or better, three, determinations of the solubility of the second substance at different temperatures. The formula used for this purpose is one analogous to that employed by Ramsay and Young for the calculation of vapour pressures, and has the form $T_1/T_1' = T_2/T_2' + c(t' - t)$, where T_1/T_1' and T_2/T_2' denote the absolute temperatures at which the two substances have the same solubility, c is a constant, and t' and t are the temperatures at which one of the substances has the solubility corresponding to the absolute temperatures T_1 and T_2 or T_1' and T_2' . This formula has been employed in the present case for calculating the solubilities of the above substances between 0° and 25° , and between 60° and 100° (in the case of anthracene and picric acid, in benzene up to the boiling-point of the latter).

120. "Menthyl Formylphenylacetate." By J. B. COHEN and S. H. C. BRIGGS.

A short time ago, the authors commenced a similar investigation to that of Lapworth and Hann (*Proc. Chem. Soc.*, xviii., 144) with the object of studying tautomeric changes by means of optically active substances, in the course of which they prepared menthyl formylphenylacetate described by Lapworth and Hann. As the authors do not intend, under the circumstances, to pursue this line of inquiry, they desire to record their observations, which, though they confirm on the whole the results given in the paper referred to, show some slight differences. Menthyl formylphenylacetate was prepared as follows:—Sodium was allowed to act on a mixture of menthyl acetate and ethyl formate dissolved in dry ether. In this reaction, an interchange occurs to some extent between the menthyl and ethyl groups, so that some menthyl formate, and some ethyl formylphenylacetate are produced. The product was poured into water, the ethereal layer removed, and the aqueous portion acidified and shaken out with ether. The ether was evaporated in a vacuum, and crystals of menthyl formylphenylacetate separated on standing. The menthyl ester thus obtained was in the form of large, well-formed, tetragonal crystals consisting of four-sided prisms terminated by pyramids; purified by re-crystallisation from chloroform, it melted at $82-84^{\circ}$ (L. and H. give $82-83^{\circ}$). The specific rotation of a freshly prepared chloroform solution containing about 3 grms. of substance in 100 c.c. is $[\alpha]_D^{18^{\circ}} = -72.6^{\circ}$ (L. and H. give -74.6°). In an alcoholic solution containing 2 grms. in 100 c.c., the specific rotation was $[\alpha]_D^{18^{\circ}} = -63.9^{\circ}$ (L. and H. give

-64.9°). The addition of sodium ethylate did not affect the rotation. The following were the effects of an alcoholic solution of ferric chloride on the substance when dissolved in various solvents. A faint violet colouration was produced in methyl and ethyl alcohol, ether, and light petroleum. No colouration was produced at first in benzene, chloroform, or ethyl acetate, but slowly developed. Menthyl phenylacetate, obtained in the preparation of the formylphenylacetate, is a colourless and odourless liquid which boils at 216° (39 m.m.).

*121. "Transformation of Diacetanilide into Aceto-p-amino acetophenone." By F. D. CHATTAWAY.

A large number of derivatives of primary aromatic amines in which various atoms or groups are attached to the nitrogen readily undergo intramolecular transformation and form isomerides in which the atom or group is attached to the nucleus in the para- or ortho-position. The best known examples of such changes are those in which a halogen atom, a nitro-group, a sulphonic group, or a hydroxyl group passes on to the ring. So far, however, the commonest substituting group in amines, the acetyl group, has not been observed to wander. The author described experiments in which this group passed into the ring in the normal manner. The substance studied was diacetanilide, which underwent transformation into aceto-p-aminoacetophenone.

122. "Nitrogen Chlorides and Bromides Derived from Ortho-substituted Anilides." By F. D. CHATTAWAY and J. M. WADMORE.

Nitrogen halogen derivatives of orthochlorobenzanilide and orthobromobenzanilide, which have not hitherto been described, are easily obtained by treating the corresponding anilides with an excess of hypochlorous or hypobromous acid, the actions, as in other similar cases, being reversible. The nitrogen chlorides and bromides so obtained show all the typical nitrogen halogen group reactions, and readily undergo transformation into the isomeric 2:4-disubstituted anilides.

The following compounds have been prepared:—

Benzoyl o-chlorophenyl nitrogen chloride,—



colourless, six-sided plates, m. p. 94° ; Benzoyl-o-chlorophenyl nitrogen bromide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NBr}\cdot\text{COC}_6\text{H}_5$, short prisms of a deep yellow colour, m. p. 110° . o-Bromobenzanilide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{COC}_6\text{H}_5$, colourless rectangular plates, m. p. 116° . Benzoyl-o-bromophenyl nitrogen chloride, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NCl}\cdot\text{COC}_6\text{H}_5$, colourless, transparent prisms, m. p. 85° . Benzoyl-o-bromophenyl nitrogen bromide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NBr}\cdot\text{COC}_6\text{H}_5$, yellow, six-sided, rhombic prisms, m. p. 99° . Acetyl-o-chlorophenyl nitrogen bromide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NBr}\cdot\text{COCH}_3$, pale yellow, four-sided prisms, m. p. 152° . Acetyl-o-bromophenyl nitrogen chloride, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NCl}\cdot\text{COCH}_3$, colourless, four-sided prisms, m. p. 86° .

123. "Substituted Nitrogen Chlorides containing the Azo-group." By F. D. CHATTAWAY.

In order to determine the effect of an azo-group on the properties and direction of transformation of nitrogen chlorides, a number of such compounds have been prepared from aminoazobenzene. Aminoazobenzene yields well crystallised acetyl propionyl and benzoyl derivatives, which react with hypochlorous acid very readily, and form nitrogen chlorides possessing all the characteristic properties of the nitrogen halogen group. This adds another to the many reasons for regarding aminoazo-compounds as primary amino-derivatives.

The following compounds have been prepared:—

p-Acetylchloroaminoazobenzene,—



orange red plates, m. p. 113.5° . Propionyl-p-aminoazobenzene, $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COC}_2\text{H}_5$, large, orange-red plates, m. p. 170° . p-Propionylchloroaminoazobenzene,

$C_6H_5 \cdot N:N \cdot C_6H_4 \cdot NCl \cdot COC_2H_5$, red prisms, m. p. 57° .
Benzoyl-p-aminoazobenzene,—



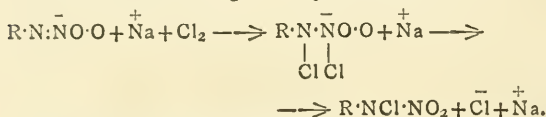
reddish-orange plates, m. p. 211° . *p-Benzoylchloroaminoazobenzene*, $C_6H_5 \cdot N:N \cdot C_6H_4 \cdot NCl \cdot COC_6H_5$, red-brown, glistening, flattened prisms, m. p. 144° .

124. "The Action of Chlorine and Bromine on Nitroaminobenzenes. Part I. s-Trisubstituted Chloronitroaminobenzenes." By K. J. P. ORTON.

In the course of an investigation of the conditions under which the nitroamines derived from s trisubstituted anilines (*Proc. Soc. Chem.*, xviii., 111) are transformed into substances containing the nitro-group in the benzene nucleus, the action of chlorine and bromine on these substances was studied.

When chlorine is passed into an aqueous solution of the sodium salt of a nitroamine, or when dilute aqueous bleaching-powder is slowly added to a solution of the nitroamine in acetic acid, the chloronitroamine is formed; thus 1-nitroamino-s-trichlorobenzene yields 1-chloronitroamino-s-trichlorobenzene, $C_6H_2Cl_3 \cdot NCl \cdot NO_2$.

As the sodium (and other) salts of the nitroamines may probably be represented by the formula $R \cdot N:N \cdot NO \cdot ONa$, and, if so, would be the salts of a substituted "imino-nitronic acid" (compare Bamberger, *Ber.*, 1902, xxxv., 54), the author suggested that the reaction of chlorine with the sodium salt might be represented thus:—



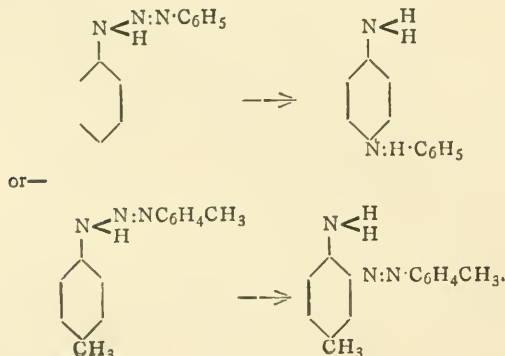
All these chloronitroamines are very unstable, and are re converted by all reagents into the nitroamines. The following compounds, all of which crystallise in lustrous, colourless prisms, have been prepared:—

1-Chloronitroamino-s-trichlorobenzene, m. p. $53-54^\circ$; 1-chloronitroamino-s-tribromobenzene, m. p. 61° ; 1-chloronitroamino-4-chloro-2:6 dibromobenzene, m. p. 56° ; 1-chloronitroamino-2:3:4:6-tetrabromobenzene, m. p. $61-62^\circ$; 2-chloronitroamino-3:5-dibromotoluene, m. p. 60° ; 4-chloronitroamino-3:5-dibromotoluene, m. p. $50-51^\circ$.

By the action of bromine on aqueous solutions of the sodium salts of the nitroamines, the bromonitroamino-derivatives are formed, but have not been obtained free from the nitroamine.

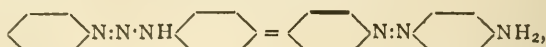
125. "The Transformation of Diazoamido- into Aminoazo-compounds and of Hydrazobenzene into Benzidine." By F. D. CHATTAWAY.

The transformation of diazoamido- into the isomeric aminoazo-derivatives is similar in nature to the other well-known transformations in which atoms or groups of atoms pass from the nitrogen of an amino-group, attached to a benzene nucleus into the para- or ortho-position in the ring, thus:—



As is usual in these intramolecular changes, the para-position is taken up by preference, the ortho-position to a less extent, or exclusively when the para-position is already occupied.

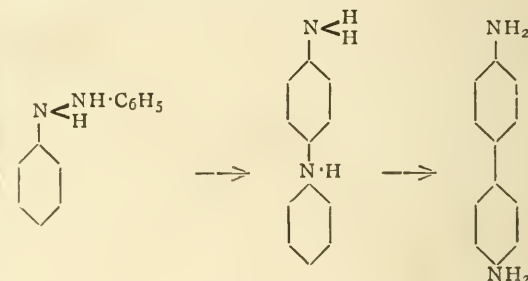
This analogy is somewhat obscured by the ordinary method of representing the transformations,—



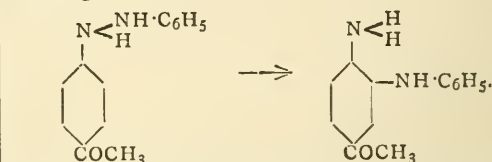
where the NH group appears to leave the chain and pass into the ring.

The formation of the various azo-derivatives which are obtained by heating diazoamido-compounds with aromatic amines and their hydrochlorides, is thus rendered intelligible without assuming the formation of intermediate nitrogen halogen compounds (Goldschmidt and Bardach, *Ber.*, 1892, xxv., 1376). It is only necessary to assume the existence of a mobile hydrogen atom and double linkage in the diazoamido-compounds, and to admit that the diazo-group can undergo transference from the nitrogen atom of one amine to that of another, present in large excess, exactly as a chlorine or bromine atom does. Much that is known of similar isomeric changes points to the conclusion that transference from nitrogen to the ring can only take place when the nitrogen is exerting its higher valency. This may explain the advantage, in these transformations, of the hydrochloride of the base.

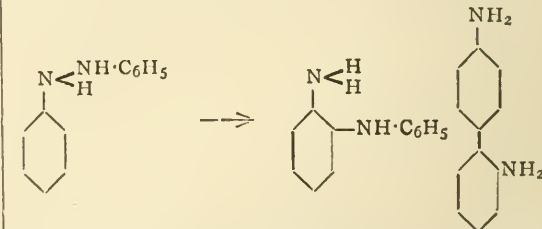
The isomeric change of hydrazobenzene into benzidine is also brought into line with other analogous transformations if similarly formulated:—



It is seen to consist of two stages, of which the first only can take place if the para-position is already occupied, the semidine and other similar transformations resulting:—



As is well known, the related ortho change also takes to some extent with the formation of diphenylene,—



in all probability, the ortho-change also takes place to a relatively very small extent in the second stage with the production of diorthoaminodiphenyl, though the latter is produced in such small quantity that it has hitherto escaped detection.

126. "Tribromophenolbromide." By E. W. LEWIS.

A re-examination of this substance has shown that the melting-point usually attributed to it (118°) is much too low, and that it may be raised to $148-149^{\circ}$ by re-crystallising the compound from ethyl acetate; moreover, whilst, as usually stated, the substance of low melting-point gives off bromine on heating at about 125° , the purified material begins to lose bromine before melting at about 145° .

The crystals of tribromophenolbromide belong to the orthorhombic system, the axial ratios being $a:b:c = 0.7945:1:1.5921$.

NOTICES OF BOOKS.

The New Volumes of the Encyclopædia Britannica. The Third of the New Volumes, being Vol. XXVII. of the Complete Work. London: *The Times*. Edinburgh: Adam and Charles Black. 1902. Pp. 744.

THE Third Volume of this work comprises those subjects which come between CHI (Chicago) and ELD (Elduayen, José de).

There are not many articles in this volume relating to chemical or scientific subjects. The "Condensation of Gases," by Prof. J. D. van der Waals, is treated mathematically and is of some interest. This article is followed by one on the "Conduction of Heat," by Prof. H. L. Callendar; it is divided into nineteen sections, such as—1. Mechanism of Conduction; 2. Law of Conduction; 5. Experimental Methods, such as the Plate method, the Tube method, Forbes's Bar method, the Guard-ring method, &c.; 13. The Periodic Flow of Heat; 15. Annual Variation, &c.

Mr James Douglas contributes an article on "Copper," dealing with its occurrence, metallurgy, and applications. "Diffraction Gratings," by H. A. Rowland, and the "Diffusion of Gases," by G. H. Bryan, are two short articles that will repay reading, while the one on "The Dynamo," by C. C. Hawkins, is of considerable importance and covers no less than twenty pages. "Earthquakes," by J. Milne, will interest many readers, as the subject is one that is attracting a good deal of attention at the present time.

The First Products of the Decomposition of Albumen in the presence of Alkalis.—O. Maas.—The author has endeavoured to find out whether, in the action of alkalis on albumen, one or several albumoses are produced, as in pepsic digestion, or in hydrolysis by weak acids. The solutions used contained 1.60 grms. to 2.25 grms. of sulphur per thousand parts, and were maintained at 15° , 40° , and 90° from one to forty-eight hours. The attack is very rapid, and when the liquid is neutralised it is observed that a mixture of albuminate (acid-albumen) and a new albumose, the *alkali-albumose*, is precipitated. The filtrate contains small quantities of albumose, but no peptone. Ovalbumen and serum-albumen behave in the same manner. The remainder of the paper deals with the description of the new albumose. It is obtained by heating 40 grms. of dry ovalbumen with 1 litre of normal soda for three or four hours on a boiling water-bath. The filtrate is treated with acetic acid so long as a precipitate is produced, and the precipitated mass gives up the new albumose to boiling alcohol. The remainder is precipitated by the addition of water, or, better still, acetone. This body is insoluble in cold water, slightly soluble in boiling water, and fairly soluble in 50 or 60 per cent alcohol. It is no more soluble in saline solutions than in water, but dilute alkalis dissolve it easily. One volume of a saturated solution of sulphate of ammonium precipitates it completely. It gives the Millon, the biuret, the Molisch (α -naphthol), and the Adamkiewicz reactions distinctly, and it blackens an alkaline solution of oxide of lead. It contains:—C, 53.57; H, 7.19; N, 13.62; and S, 2.13 per cent.—*Zeit. Phys. Chem.*, vol. xxx., p. 61-74.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxiv., No. 26, June 30, 1902.

New Researches on Liquid Silicon Hydride, Si_2H_6 .—H. Moissan and S. Smiles.—In a previous paper the authors published an account of the preparation and some of the properties of liquid silicon hydride, Si_2H_6 . They have continued this research, and give further proof of the formula Si_2H_6 . This silicide corresponds to ethane; it is spontaneously inflammable in presence of air, and possesses very energetic reducing properties. It decomposes carbon tetrachloride and sulphur hexafluoride with violence.

Certain Properties of Amorphous Silicon.—H. Moissan and S. Smiles.—When the vapour of liquid hydrogen silicide is decomposed by a series of induction sparks, hydrogen and silicon are obtained. This silicon is in a finely-divided state, and slowly reduces a neutral solution of potassium permanganate at ordinary temperatures. This reduction becomes more rapid at 100° . Various other reductions are effected by silicon prepared in this manner.

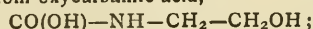
Double Nitrites of Iridium.—E. Leidié.—The author repeats Gibbs and Lang's experiments on iridium nitrites and prepares—(1) The double nitrite of iridium and potassium, $\text{Ir}_2\text{K}_6(\text{NO}_2)_{12}$; (2) the double nitrite of iridium and sodium, $\text{Ir}_2\text{Na}_6(\text{NO}_2)_{12} \cdot 2\text{H}_2\text{O}$; (3) The double nitrite of iridium and ammonium, $\text{Ir}_2(\text{NH}_4)_6(\text{NO}_2)_{12}$. By means of the chlorides of iridium and nitrites of barium, mercury, and silver, he was not able to reproduce exactly the compounds described by Lang or Gibbs.

Constitution of the Aloines. Comparison with that of the Glucosides.—E. Léger.—In a preceding paper the author showed that barbaloin and isobarbaloin, when acted upon by Na_2O_2 , give the same product of oxidation, methylisoxychrysin, and that the chlorated derivatives of these same aloines give a single tetrachlorated methylisoxychrysin. This shows that the two isomeric aloines contain a common radicle. Their properties are very similar; both yield chrysammic acid when treated with HNO_3 . When heated in a dry tube, it gives off vapours which redden aniline acetate paper. A result of the author's researches on this subject show that the aloines belong to a new class of bodies—glucosides which are not decomposed by dilute acids.

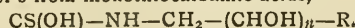
Action of Carbon Disulphide on Polyvalent Amino-alcohols.—L. Maquenne and E. Roux.—Carbon disulphide attacks the polyoxyamines when heated, giving cyclic compounds having a single atom of sulphur; these apparently belong to the family of the oxazolines. These results can be predicted from those obtained by Gabriel with bromated amines and those which were quite recently obtained by Franchimont and Lublin by condensing ethanolamine with methyl chloroformate, and so obtaining the

body $\text{NH} \begin{array}{l} \text{CH}_2-\text{CH}_2 \\ | \\ \text{CO}-\text{O} \end{array}$. Gabriel's compounds result

from the anhydriodisation of dithiocarbamic acids, $\text{CS}(\text{SH})-\text{NH}-\text{CH}_2-\text{CHOH}-\text{R}$; that of Franchimont is derived from oxycarbamic acid,—



the author's from monothiocarbamic acids,—



They consequently form a new series intermediate between the two preceding, and comparable with the substance Hofmann obtained by combining the senevols with the alcohols.

Mechanism of the Synthesis of Leucine.—A. Vila and E. Valés.—The authors describe a preparation of ammonium-valeral producing a crystalline hydrate. Under the given conditions, the action of hydrocyanic acid on this body yields a single compound, unknown up to the present time, but produced in this reaction in considerable quantity. The hydrolysis of this derivative by dilute sulphuric acid furnishes directly leucine, capable of being sublimed, and characterised by its insoluble copper salt.

MISCELLANEOUS.

Tetrabromide of Platinum.—A. Miolatti and I. Bellucci.—Platinic bromide, PtBr_4 , is slightly-soluble in water, and gives a light reddish-brown solution; the examination of this latter from the point of view of acidimetry, electrical conductivity, and the action of the salts of the heavy metals, leads to the opinion that PtBr_4 is the anhydride of a bibasic *tetrabromoplatinic acid*, $\text{PtBr}_4(\text{OH})_2\text{H}_2$. The following salts are of a deep brown colour:—Salts of silver, $\text{PtBr}_4(\text{OH})_2\text{Ag}_2$; of thallium, $\text{PtBr}_4(\text{OH})_2\text{Tl}_2$; of mercury, $\text{PtBr}_4(\text{OH})_2\text{Hg}$; and of lead (basic), $\text{PtBr}_4(\text{OH})_2\text{Pb.Pb}(\text{OH})_2$.—*Zeit. Anorg. Ch.*, v. 1. xxvi., p. 222.

Action of certain Nitrated Substances on the Coagulation of Albumen.—K. Spiro.—The albuminous solution used was beaten-up white of egg, treated with acid phosphate of potassium until the reaction was acid to litmus; it was then filtered and diluted with varying amounts of water. Mauthner has already shown that choline prevents the coagulation of ovalbumen. Piperidine exercises the same action. Bases, such as pyridine and aniline, which are precipitants of albumen, are able, nevertheless, to stop a portion of the albumen from coagulation. Orthotoluidine (but not the para derivative) and xylydine act in the same manner. Nitrated substances of a non-basic character, such as urethane, various amides (formamide, urea), and the senevols, have the same action. The explanation of this action must be sought for in the basic character of these substances, a character strongly marked in some of them, but less apparent in others. But Ostwald has remarked that we can attribute to urea in solution a formula such as $\text{CO.NH}_2\text{OH.NH}_2$, and, on the other hand, the author shows that albumen, held in solution by concentrated solutions of urea, takes all the characteristics of an alkali-albumen, and that in the coagulation of ovalbumen the urea acts decidedly as an antagonist to acetic acid.—*Zeit. Phys. Ch.*, vol. xxx., p. 182—199.

Pentachloroplatinic Acid.—A. Miolatti and I. Bellucci.—The authors have examined the bodies which result from the substitution of 1, 2, 3, &c., hydroxyl for an equal number of atoms of chlorine in chloroplatinic acid (hexachloroplatinic), PtCl_6H_2 , and are at present at work on the first term of the series, *pentachloroplatinic acid*, $\text{PtCl}_5(\text{OH})\text{H}_2$, which is no other than the product $\text{PtCl}_4.\text{HCl}.2\text{H}_2\text{O}$, prepared by M. Pigeon (*Ann. Chim. Phys.*, Series 7, vol. ii., p. 433), by heating chloroplatinic acid to 100° for two or three days in an exhausted tube containing a few fragments of potash. On repeating this experiment on a larger scale in an exhausted oven with a larger surface, and in which the potash could be renewed during the operation, they easily obtained M. Pigeon's product in the form of a reddish-brown mass, fusible on the water-bath, extremely deliquescent, and giving yellowish-brown slightly cloudy solutions with a distinctly acid reaction. These solutions are not precipitated in the cold by ammonia, which is distinctive of PtCl_6H_2 ; with KCl or NH_4Cl we get the ordinary chloroplatinates. Acidimetry and the study of the electric conductivity show that we have to deal with a bibasic acid of which several salts have been prepared. *Salt of Barium*, $\text{PtCl}_5(\text{OH})\text{Ba}_4\text{H}_2\text{O}$.—The acid is exactly neutralised by

baryta in concentrated solution; it is then evaporated in the desiccator, and gives long orange-coloured prisms. *Salt of Silver*, $\text{PtCl}_5(\text{OH})\text{Ag}_2$.—Prepared from nitrate of silver in the cold, an abundant yellowish precipitate is formed, not decomposable by boiling water; this distinguishes it from the ordinary chloroplatinate, PtCl_6Ag_2 , and shows that it is nearer the tetrachloroplatinate, $\text{PtCl}_4(\text{OH})_2\text{Ag}_2$. *Salt of Thallium*, $\text{PtCl}_5(\text{OH})\text{Tl}_2$.—This is a pale rose-coloured precipitate. *Basic Salt of Lead*, $\text{PtCl}_5(\text{OH})\text{Pb.Pb}(\text{OH})_2$.—Yellowish precipitate.—*Zeit. Anorg. Ch.*, vol. xxvi., p. 209.

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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2227.

A NOTE ON

THE RE-CRYSTALLISATION OF PLATINUM.*

By WALTER ROSENHAIN, B.A. (Cantab.), B.C.E. (Melbourne).

IN a recent paper ("On the Crystalline Structure of Metals," second paper, *Phil. Trans.*, A, 1900, vol. cxcy., pp. 279—301) Professor Ewing and the present author have described phenomena of re-crystallisation in a number of metals, such as lead, tin, zinc, and cadmium, at temperatures well below the melting-points of those metals. I have recently observed phenomena which appear to me to be of a very similar nature in the case of platinum.

blowpipe flame. A closer examination revealed a multitude of geometrical pits (Aetzfiguren) clearly demonstrating that the appearance is due to genuine metallic crystals which have been *etched* on the surface by some chemical agent. Two other experimental facts confirm this idea. The first is that if a piece of platinum showing the "changed" surface be exposed to the action of aqua regia, the appearance is intensified and brightened. If, as has been suggested, the appearance were due to a superficial layer of a platinum carbon compound from which the carbon had been driven off, leaving mere pseudomorphs of platinum, the etching action of the aqua regia would have dimmed the appearance instead of brightening it. Another objection to the carbonisation theory is to be found in the fact that I have produced the effect on a *new* platinum crucible by prolonged heating in an oxygen injector furnace, where an oxidising atmosphere was being maintained.

The "changed" platinum is, moreover, very weak and brittle when hot, and on one occasion a crucible was torn whilst still red hot, but after being removed from the flame. The fracture was as crystalline as that of

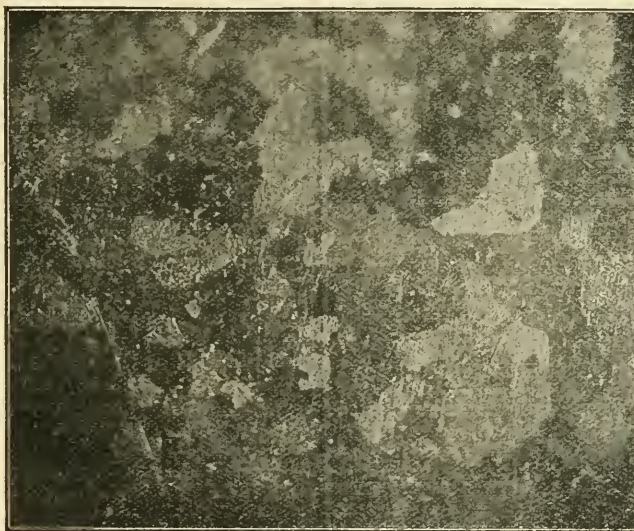


FIG. 1.—SURFACE OF A PLATINUM CRUCIBLE AFTER PROLONGED HEATING.
(Oblique Light. Magnification, 30 diameters*.)

It is a well-known fact that a prolonged exposure to a high temperature renders platinum brittle, and that the surface of such platinum, when it has been exposed to flame, shows markings "resembling the appearance of galvanised iron" ("The Action of the Acetylene Flame on Platinum," J. J. Redwood, *Journ. Soc. Chem. Industry*, vol. xvii., p. 1107; also *Zeit. für Analyt. Chem.*, 1901, Heft 6, p. 411). This phenomenon has generally been ascribed to the action of carbon, and by one author specifically to the action of acetylene (*Ibid.*). Having studied the phenomena closely with the aid of the microscope, I do not find this view entirely confirmed.

In the first place, on examining the surface of the "changed" platinum with the microscope, it is seen to show a pattern which is characteristic of the *etched* surface of a crystalline metal. The micrographic appearance under oblique light is shown, magnified 30 diameters, in the photograph (Fig. 1). This was taken from the surface of a platinum crucible which has been in continuous use, and is frequently exposed for hours together to an ordinary

"brittle" zinc, and the lines of fracture ran across the crystals revealed on the changed surface in such a way as to show that these crystals seen on the surface are not a thin superficial layer, but genuinely represent the entire structure of the metal.

I am therefore led to the conclusion that the action is simply one of re-crystallisation. The metal in the state in which it reaches us in foil or crucibles, &c., is in a condition of severe strain, having been bent, drawn, rolled, &c., either in the cold or at temperatures far below its "annealing" temperature. This is supported by the fact that the platinum in its "unchanged" state shows a very minute structure characteristic of severely strained metals. The natural effect of exposure to a high temperature of metal in such a condition is to allow it to re-crystallise, and this I conceive to be what occurs in the case of platinum. The brittleness of the "annealed" metal is not at all surprising, as the same phenomenon occurs with zinc and cadmium (see paper cited above). In the case of platinum "annealed" in a gas flame there is, however, a further action; simple annealing or re-crystallisation, although it will completely alter the interior structure of

* A Paper read before the Royal Society, May 15, 1902.

a piece of metal, will not of itself alter the appearance of the surface even in microscopic detail. To develop a surface pattern corresponding to the changed internal structure the surface must be etched after the re-crystallisation has taken place. The etching action is in this case undoubtedly due to the gases of the flame, and the temporary formation of a carbide may play a part in this process.

SOME REMARKS ON A. BACH'S PAPER, "THE MECHANISM OF THE ACTION OF PEROXIDE OF HYDROGEN ON PERMANGANIC ACID,"

IN SO FAR AS IT INVOLVES THE QUESTION
OF THE VALENCY OF HYDROGEN.

By GEOFFREY MARTIN, B.Sc. (Lond.).

WITH regard to the main part of the paper (*Moniteur Scientifique*, January, 1902, Series 4, vol. xvi.) I have nothing to say. It involves a point that must be settled by experiment.

But I take exception to his remark:—"To admit, as is done by Traube, that peroxide of hydrogen contains easily oxidisable hydrogen united directly with active oxygen seems contrary to reason."

For my part I fail entirely to see that such an assumption is contrary to reason. It is true that it involves the supposition that a hydrogen atom can combine with more than one atom at the same time—in other words, can act as a polyvalent element. But in support of this view there is a great body of experimental facts slowly accumulating.

A brief review of this evidence will perhaps be useful, as outside a special circle the majority of chemists still seem to regard hydrogen as the stock instance of a monovalent element.

When a hydrogen atom enters into combination with an atom more negative than itself, such as O or Cl, it almost invariably acts as a monad.

At the time the valence theory was broached these were practically the only class of hydrogen compounds known, and it was for this reason that this element was labelled "monad."

But an entirely new class of compounds have within recent years come to light. They are produced by the union of hydrogen with elements more positive than itself; and in these compounds it no longer acts as a monad, but appears often to be playing the part of a polyvalent element.

The following are a few of these compounds:—

Na_2H .—Soft wax-like substance, formed at 300° and dissociated at 421° . (Troost and Hautefeuille, *Comptes Rendus*, lxxviii., 807).

K_2H .—White saline crystalline compound. (Raoult, *Comptes Rendus*, lxi., 826).

(In these two compounds the minimum value we can ascribe to H is 2).

$\text{FeH}_2(?)$.—Black powder, like finely divided iron; evolves H on heating and on treatment with H_2O . Formula conjectural, as it has not yet been analysed. (Ramsay, "System. Chem.," 1891, p. 575).

Pd_2H .—According to Ramsay (*loc. cit.*), "The alloy approximates in composition to that expressed by the formula Pd_2H , but it appears to absorb hydrogen in excess, which is not chemically combined, but in a state of mixture." Now palladium only forms two classes of compounds—the palladous, in which it is divalent, and the palladic, in which it is tetravalent. Therefore the lowest valency H can have here is 4 and the highest 8.

NbH .—Black powder. (Krüss, *Ber.*, xx., 169). Since niobium acts invariably as a quinquevalent element, the value H can have here is 5.

Vd_3H_2 .—Vanadium can act as a monad, dyad, triad, or pentad element. If it acts as a monad in the above compound the valence of H would not be a whole number. If it acted as a dyad, the value of H comes out as 3.

CuH .—Black powder, decomposes between 55° and 60° . (Wurtz, *Annales*, [3], xi., 251). If Cu be here in a cupric state, H is divalent; if in a cuprous state, H is monovalent.

Traces are met with of a great many others, but in the majority of cases they are very imperfectly known.

It would appear that in these hydrogen can act respectively as a monad, dyad, triad, tetrad, and pentad element.

The fact that these compounds are unstable and rare has nothing whatever to do with the validity of the conclusions to be drawn from the behaviour of hydrogen in them.

Under other conditions, a rare and unstable compound may become common and stable, and a stable common compound rare and unstable. For instance, were there little oxygen on the earth, H_2O would be a very rare compound; and did we live at a temperature of 4000°C ., it would, in addition, appear to us as an extremely unstable body, easily decomposable into H and O gases. In fact, under such conditions, it would rank in our estimation as do some of the hydrides at ordinary temperatures. But its scientific significance would be quite as great under these as under normal conditions.

Similarly, did we live in an atmosphere of hydrogen—such as exists in some stars—and under a great pressure and temperature, the hydrides would probably be very prominent and abundant bodies.

Their existence, therefore, cannot be ignored; and the rôle of hydrogen in them demands an explanation with as great a force as if they were the most prominent section of the hydrogen compounds.

In this connection it is interesting to note that definite halogen compounds of potassium, rubidium, and caesium are known in which the metal plays a monad, triad, and pentad rôle.

Thus, of the type RX_3 , we know—

KI_3 ;
 RbBr_3 , RbI_3 , RbClBr_2 , RbCl_2Br , RbBr_2I , &c.;
 CsBr_3 , CsI_3 , CsClBr_2 , CsCl_2Br , CsClBrI , &c.;

and of the type RX_5 , we have—

KICl_4 ;
 RbCl_4I ;
 CsBr_5 , CsI_5 , CsCl_4I .

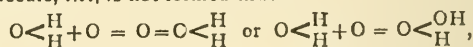
Towards oxygen and sulphur they also appear to be able to act as divalent and tetravalent elements.

It will not be, therefore, very surprising if hydrogen, which belongs to the odd series of Group I., is also found to be capable of acting as a polyvalent element in certain rare cases.

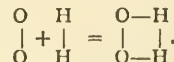
If we assume that in hydrogen peroxide it is acting with a valency of 2, and that this compound has the constitution

$\begin{array}{c} | \quad | \\ \text{O}-\text{H} \end{array}$, we get a perfectly clear interpretation of the fact,

so ably demonstrated by Traube, that hydrogen peroxide is not an oxidised water molecule, but a reduced oxygen molecule, *i.e.*, is not formed thus—



but is formed thus—



It may be noted that it is almost certain, both from its physical and chemical behaviour, that this compound does not contain hydroxyl groups.

We have pointed out that when electro-positive hydrogen enters into combination with an electro-negative element, it usually acts as a monad; but when it combines with an element of positive polarity, it appears to behave as a polyvalent element.

This appears to be quite a general phenomena. For instance, when the negative halogens combine with positive radicals, they invariably act sharply as monads. But when they enter into combination with radicals of like sign, they no longer act as monads, but exhibit a poly-

valent nature, e.g., in ICl_3 , $\text{I} \begin{matrix} \nearrow \text{C}_6\text{H}_5 \\ \nearrow \text{C}_6\text{H}_5 \\ \searrow \text{OH} \end{matrix}$, &c.

The metals, too, when they unite with each other, give rise to phenomena of an essentially similar nature. They appear to act towards each other with a quite different valence to that with which they usually act towards negative radicals. For instance, there are known to exist definite compounds of the formulæ AuCd , PtAl_3 , Au_4Pb , Au_5Pb_2 , SnSb , and many others much more complex (see Nevill, "Report on the Nature of the Compounds contained in Alloys," British Association, 1900).

So that if it is ultimately found that electro-positive H enters into union with an electro-positive element, it will at least have a precedent in the case of actually known elements.

A. Bach's assertion, therefore, that "to admit that . . . hydrogen peroxide contains easily oxidisable hydrogen united directly with active oxygen seems contrary to reason," is by no means self-evident; but, on the other hand, it appears that the facts speak strongly for the view that in certain cases hydrogen is capable of combining with more than one atom at the same time.

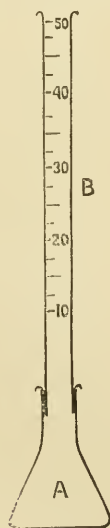
University of Berlin, May 26, 1902.

APPARATUS FOR DETERMINING MINERAL OIL IN A MIXTURE OF MINERAL AND VEGETABLE OILS.

By R. F. YOUNG and B. F. BAKER.

WE beg to submit the accompanying apparatus for rapidly and accurately determining the per cent of mineral oil in a mixture of mineral and vegetable oils.

Into the flask A is ground an accurately graduated glass tube, holding about 60 c.c. of liquid and graduated to one-



tenth c.c. To use the apparatus 50 c.c. of the oil under examination is measured into A, excess of alcoholic potash added, and the oil saponified by heating on the water-bath in the usual way with a reflux condenser or simply a long glass tube, which may also be ground to fit

A. When saponification is complete, the flask is fitted with B, and water added till the unsaponified oil rises into the graduated tube. The volume of oil is then read off. Then $\frac{\text{Volume of oil in tube}}{50} \times 100 = \text{per cent of mineral oil in sample.}$

The Laboratory,
Wouldham Cement Company (1900),
West Thurrock, Essex.

NOTES ON COCOA ESSENCES.

By E. G. CLAYTON, F.I.C.

THERE are very few published determinations of the cocoa-starch or of the caffeine, as well as theobromine, present in "cocoa essences" (cocoas deprived of a part of the fat, and otherwise treated). The following analyses, which in most cases include these details, may therefore be useful for reference:—

Numbers 4 and 5 contained minute quantities of foreign starches, so that the starch in the former was nearly—but not quite—all cocoa-starch. Some of the caffeine also in No. 4, and the maltose, were extraneous. Considerable variations are observable in the proportions of cellulose and soluble alkali in these preparations of cocoa. Bell's process was used for the determinations of theobromine and caffeine; and starch was determined, after removal of the fat, alkaloids, and carbohydrates soluble in cold water, by conversion into dextrose and titration with Fehling's solution (10 dextrose = 9 starch). Protein nitrogen was Kjeldahlised after extraction of the alkaloids.

	Sample.				
	1.	2.	3.	4.	5.
Water	4'62	3'22	3'59	5'33	4'28
Fat	33'11	32'69	30'50	22'30	27'46
Theobromine	1'82	0'93	0'88	0'83	2'69
Caffeine	0'08	0'02	0'42	0'66	0'16
Starch	5'63	6'56	—	5'06	—
Proteids	15'56	14'31	14'19	19'50	12'12
Maltose	—	—	—	1'64	—
Cellulose	5'65	9'29	6'97	5'59	4'21
Cocoa-red, dextrin, tannin, &c. .. .	27'82	25'15	37'35	32'47	42'77
Ash	5'71	7'83	6'10	6'62	6'31
	100'00	100'00	100'00	100'00	100'00
Soluble ash	3'20	7'44	5'67	4'67	3'13
Insoluble ash .. .	2'51	0'62	0'43	1'81	3'18
Alkalinity (as K_2O) of soluble ash ..	1'16	2'94	2'21	1'48	0'86
Total phosphoric acid (P_2O_5)	1'91	1'72	1'93	1'92	1'29
Soluble phosphoric acid	—	—	—	—	1'15
Insoluble phosphoric acid	—	—	—	—	0'14
Silica	—	0'36	—	0'69	—
Iron oxide	—	trace	—	0'32	—
Proteid nitrogen ..	2'49	2'29	2'27	3'12	1'94
Cold water extract (total)	17'90	17'20	14'56	18'25	—
Cold water extract (organic)	15'10	12'30	10'48	13'29	—
Alkalinity of cold water extract ..	2'76	3'39	2'72	2'75	—
Ash of cold water ex- tract	2'80	4'90	4'08	4'96	—

Chemical Laboratory,
32, Holborn Viaduct, London, E.C.,
July 15, 1902.

ON RADIO-ACTIVE BISMUTH (POLONIUM).

(PRELIMINARY COMMUNICATION).

By W. MARCKWALD.

In the year 1898 P. and S. Curie were induced, by Becquerel's beautiful observations on the peculiar radiation of uranium minerals and preparations, to submit the pitchblendes to a searching chemical examination. Thus they found, in extremely small quantity in these minerals, two exceedingly interesting constituents, which were radio-active in a far higher degree than the uranium compounds.

The substance which was first discovered gave all the chemical reactions of bismuth, and differed from it only in radio-activity, which was about a hundred times that of pitchblende. By partial sublimation of the sulphide, partial precipitation of the nitrate by means of water, &c., the metal, in the form of the compounds in question, could be decomposed into inactive bismuth derivatives on the one hand, and, on the other, into about four times as much of compounds of radio-active bismuth. Although the discoverers had no doubt that the final product consisted essentially of bismuth only, they did not succeed in increasing the proportion of the active constituent. They suggested Polonium as the name of the unknown element which was supposed to be the cause of the activity.

The discovery of radium soon followed that of radio-active bismuth. The authors were more fortunate in their attempts to separate radium from barium. For, by crystallisation of the chloride, they succeeded in freeing the radium almost entirely from the barium, though they could not obtain it perfectly pure. I have recently described how, by a specially adapted method of crystallisation, the separation of the barium from the chloride containing radium can be brought to any degree of perfection.

The further examination of these radio-active substances, to which were soon added others—actinium, europium, radio-active lead,—brought to light a striking difference between the activity of radium and that of polonium, namely, while the activity of freshly separated radium preparations at first increased strongly and finally became constant, F. Giesel observed that his radio-active bismuth, for the most part, lost its activity after some weeks, and Curie's preparation exhibited the same phenomenon, though more slowly. This led Giesel to the supposition that, "in polonium, we have before us probably nothing more than bismuth made active by induction." For it has been proved repeatedly that radio-active substances can transfer their activity to other substances, especially if the latter are precipitated from a solution containing active substances.

The discoverers of polonium lately seem to have adopted Giesel's opinion. At any rate, an article by P. and S. Curie which has recently appeared contains in a footnote the sentence:—"Polonium is a species of active bismuth; there is as yet no proof that it contains a new element."

Observations which I have made during the examination of radio-active bismuth have already elucidated in some respects the nature of this substance. In order to secure to myself the undisturbed continuation of these experiments, the preliminary results are here shortly described.

In the autumn of last year some kilograms of a by-product obtained from pitchblende were sent to me for examination by the firm of Dr. Richard Sthamer, of Hamburg. According to information supplied to me, the material formed the residue which remained after treatment of pitchblende with concentrated sulphuric acid and washing with water. The aim of the research was first to determine whether radio-active substances could be obtained from the material, and finally to work out a method which could be used technically for the separation of these substances.

The material was comparatively rich in radio-active bismuth. By already known methods, about 1 per cent by weight of bismuth oxychloride could be obtained from the raw material. The product was strongly radio-active. No decrease in the activity has been observed after the lapse of several months.

Many attempts were made to separate a radio-active constituent from this substance; some were unsuccessful, and some gave unsatisfactory results, which still remain to be further investigated. Finally, the problem was successfully solved by a very simple method.

Starting from the assumption that, in radio-active bismuth, besides ordinary bismuth, a second radio-active metal is present, which very closely resembles the first in its chemical reactions, the behaviour of the salts on electrolysis was examined. If the two metals exhibited any difference of potential whatever—and this was to be expected from the great analogy in chemical behaviour—this must become apparent on electrolysis, so that either the active or inactive constituent would increase in the metal which first separated out. An experiment was performed under quite arbitrarily chosen conditions, and the result showed that the metal which separated out first exhibited a much greater activity than the final product. This result led to an attempt to directly replace in the hydrochloric acid solution of the chloride the ions of the radio-active metal by bismuth ions, by immersing a polished stick of bismuth in the solution.

As was to be expected, the metal became coated immediately with a fine black deposit, which increased visibly in a few hours. When taken out of the solution and washed with hydrochloric acid and alcohol, the stick had a surprisingly strong effect on the electroscope. At a distance of a decimetre the leaves of the charged electroscope collapsed in a moment, and even a gutta-percha rod which had been well rubbed with fur was at once discharged on the approach of the bismuth stick.

The fact that all the radio-active metal is deposited on the bismuth stick in the course of a few days is of the greatest importance. When 8 grms. of bismuth oxychloride, in a hydrochloric acid solution, were allowed to stand for three days with a small plate of bismuth, the salt in the solution was practically inactive. To confirm this a new stick of bismuth was left in this solution for twenty-four hours; it remained perfectly clean, and was only very slightly radio-active.

The deposit could be easily and almost entirely scraped off the bismuth plate; it weighed about 5 m.grms. Hence radio-active bismuth contains probably at the most one-tenth per cent of the radio-active metal. Therefore a ton of pitchblende would contain roughly not more than 1 gm.

The substance is not the pure metal, but contains some chlorine. On heating, a small portion volatilises, probably in the form of chloride. The residue fuses to a white shining metallic bead, which is exceedingly brittle. It is easily soluble in nitric acid. As far as the solution has yet been examined for bismuth, it gives the characteristic reactions of that metal. Nevertheless, the metal cannot be identical with bismuth, for the separation of a metal of its own accord from a solution would violate the law of conservation of energy, except in cases of the formation of concentration currents, which is impossible in this instance.

The rays emitted from the metal, and equally strongly from the salts as well, are characteristically different from those of radium, for they seem unable to penetrate any intervening substance. If a stick of bismuth, prepared according to the above method and having a strong effect on the electroscope, be merely lightly wrapped in filter-paper, it loses all its effect.

This feeble power of penetration of the rays is also the cause of the fact that no appreciably stronger effects are obtained by the use of thicker deposits than those of about a ten-thousandth of a gm. The firm of Dr. Richard Sthamer intends to bring into the market such little sticks for use in physical researches and demonstrations.

My next task will be to obtain enough of the new metal to carry out an atomic weight determination. The above-named firm, which has most kindly done much to facilitate my researches, has, by following my instructions, obtained in their factory bismuth from pitchblende in large quantity, and also radium; and I owe them my hearty thanks for sending me almost 1 kilo. of bismuth oxychloride. I hope to be able to attain the desired end with this quantity.—*Berichte*, 1902, xxxv., 355.

EXPERIMENTAL RESEARCHES ON THE CONSTITUTION OF CRYSTALS.*

By A. E. TUTTON, B.Sc., F.R.S., F.C.S.

(Concluded from p. 43).

THERE will now be introduced to you another means which we possess of determining the position and shape of the ellipsoid. In an ellipsoid having three unequal rectangular axes, it will be evident that if we consider the elliptical section containing the maximum and minimum axes, there must be a point somewhere on each elliptical quadrant where the radius vector will be equal to the intermediate axis. Such are the four points C on the figure projected on the screen. The two sections of the ellipsoid which contain these points and the intermediate axis will consequently be circles, and rays of light which pass through the crystal at right angles to these sections will be able to vibrate with equal velocity in all directions perpendicular to the line of propagation. Consequently in these two directions, which are termed optic axes, the crystal will exhibit no double refraction. When the Y velocity approaches nearer to the X velocity the inclination of the two circular sections to each other naturally diminishes, and the angle between the optic axes becomes proportionally less, until at length we have equality of X and Y, the ellipsoid becoming a spheroid, with a single optic axis. This is the special case which we observe in tetragonal and hexagonal crystals, such as the well known cases of calcite and quartz.

We will now see some very beautiful phenomena in connection with these optic axes, employing for the purpose a projection polariscope, which is furnished with a special set of lenses to render the light strongly convergent while passing through the crystal. First let us investigate the phenomena exhibited by one of the uniaxial crystals we have just referred to. A section-plate cut perpendicular to the single optic axis is now between the crossed Nicols, and you see the beautiful spectrum rings and the black cross, characteristic of uniaxial crystals, which are produced.

We will next see the effect produced by a section-plate of a biaxial crystal, similar to the salts we are discussing. The plate is cut perpendicular to that axis of the ellipsoid which is the bisectrix of the acute angle between the optic axes. You observe the loci of the two optic axes are marked by hyperbolic brushes, in the present position of the section, and they are surrounded by separate rainbow-coloured rings, which in turn are surrounded by lemniscates, and eventually ellipse-like curves. If we rotate the section 45° , the hyperbolæ join up to form a cross, but the loci of the optic axes remain marked by the rings. These rings are large and brilliant, to render the demonstration clear, and are afforded by a very large section-plate. But for research purposes we require the rings to be very small and the hyperbolæ very narrow, so that the measurement of their position may be very accurate.

We will put in another section-plate, much smaller because of the impossibility of obtaining larger ones, of rubidium magnesium selenate, and you see how small and sharp, although naturally fainter, the rings and hyperbolæ are.

Next let us demonstrate how we measure the angle of separation between the two optic axes. Another section-plate has been arranged on a small goniometer, so that it can be rotated in the plane of the axes. You see we are able to bring first one and then the other optic axis up to the cross wires, which you see also focussed on the screen.

If we note the reading of the goniometer circle while one optic axis is so adjusted, and then rotate until the other is in position and read the circle again, the difference between the two readings will give us the apparent angle between the axes as seen in air.

In order to arrive at the true angle within the crystal, it is necessary to cut another section perpendicular to the bisectrix of the obtuse angle between the axes, and to measure this obtuse angle. As, however, this large angle is usually invisible in air, owing to internal reflection, it is necessary that both angles shall be measured while the sections are immersed in some highly refractive liquid. A simple calculation, involving the two angles measured, enables us then to deduce the true optic axial angle within the crystal.

The result of a large number of such measurements of optic axial angles has been to show that in all cases where the interference figures are normal, the angle of the rubidium salt is intermediate in value between the angles of separation of the optic axes of the potassium and cesium salts of the same triplet.

We will conclude the lecture by demonstrating to you the beautiful optic axial phenomena in the four abnormal cases to which reference was made when discussing the refraction phenomena, in which for a certain wave-length of light a prism of the crystal only gives one refraction image instead of two.

You see on the screen the type of interference figure which is given by rubidium sulphate. It is characteristic of the few known interesting salts which exhibit the phenomenon of crossed axial plane dispersion.

You see next the interference figure afforded by cesium magnesium selenate. It is characterised by large dispersion, and it will be proved to you in a moment that for blue light this crystal also is apparently uniaxial, and that the figure in white light which you are now contemplating is due to the fact, that for the most luminous colours of the spectrum separation of the optic axes in the horizontal plane occurs.

It would be interesting to analyse this figure by showing you the curves afforded by the crystal in the pure monochromatic light from the spectroscopic illuminator. But although this can be done most brilliantly for one person at a time looking through the so illuminated observing instrument, there is not light enough for projection. But a series of six photographs, for six specific wave-lengths of light, have been taken with the aid of the apparatus, and you now see them on the screen, each with as exact a reproduction of the colour for which it was taken as possible. The first shows the separation for red lithium light, the second the diminished angle for yellow sodium light, the third the still smaller angle for green thallium light, the fourth the further approach towards the centre for greenish blue hydrogen light, the fifth shows the uniaxial figure in light of wave-length 466 for which crossing occurs, and the sixth shows the separation in the perpendicular plane for violet hydrogen light.

We will also show you another six, to prove to you that not only does change of wave-length in the illuminating light provoke extraordinary changes in the optic axial angle, but that change of temperature is also provocative of remarkable changes of angle. This set represents the phenomena observed at about 80° . The angle for lithium light is now very much smaller than it was at the ordinary temperature; for red hydrogen light it is still smaller, and for sodium light the crossing has now actually arrived, while for thallium green, hydrogen greenish-blue, and the blue light for which crossing occurred at the ordinary temperature, the axes are separated at increasing angles in the perpendicular plane.

* A Lecture delivered at the Royal Institution of Great Britain, Friday, May 2, 1902.

Our last experiment will illustrate the effect of change of temperature in the case of caesium selenate. The behaviour of this salt is so similar to that of the long-known case of gypsum, that, as I can obtain a very much larger crystal of this beautiful mineral, suitable for projection purposes, I shall use it to demonstrate the phenomena. You see at the ordinary temperature nothing whatever beyond the fact that some light gets through to the screen. The optic axes are at present separated in the horizontal plane to such an extent that they are well outside the field. We are now warming the crystal, and you see colour making its appearance at the sides; now the axes themselves, surrounded by their coloured rings, are appearing. They approach the centre, they now coalesce to form the uniaxial cross and spædum circles. They now separate in the vertical plane, and we remove the source of heat, the axes still continuing to separate vertically until the crystal and the metal frame in which it is being heated have taken up the same temperature. Now the motion stops, and the phenomena repeat themselves in the inverse order, once more coming to a cross and circles, and again separating in the horizontal plane, until finally they disappear on the margin of the field.

These beautiful cases of crossed axial plane dispersion, you will remember, are entirely due to the operation of the rule which we found to govern the progress of the double refraction, in accordance with the progress in the atomic weight of the alkali metal, so that these very exceptional cases are in reality strong proofs of the main generalisation derived from this work.

It has thus been amply demonstrated to you that the chief result to which these researches have led is, that the members of every series of salts known to the chemist, which differ by containing different elements of the same family group, exhibit perfectly regular variations in their exterior morphology and in their interior physical properties; and that these variations follow the order of the differences between the atomic weights of those interchangeable elements. Thus, it has been shown that the crystallographical properties of the elements are in line with their other properties, chemical and physical, in exhibiting the same progressive character which is so conveniently expressed by their atomic weights.

We do not yet know why a particular series of salts chooses the specific type of symmetry which is common to its members, but we have reasonable ground for hope that further work in the direction indicated, together with a successful development of the interesting mathematical and geometrical researches now being conducted by several fellow-workers, on the possible modes of partitioning space and the types of molecular packing, will eventually lead to a solution of this important question.

During the researches described in this lecture many thousands of crystals have had to be prepared in a state of perfection and purity, many hundreds of section plates and prisms cut and ground, and innumerable measurements with the most refined of instruments carried out. But one forgets the labour in the contemplation of knowledge truly gained, and one remembers only the delights of the way, the glorious phenomena of colour which one has enjoyed, and the exquisite beauty of the crystals themselves.

ON AMMONIO-CALCIC PHOSPHATE.

BY HENRI LASNE.

I FIRST obtained ammonio-calcic phosphate in 1894, and I mentioned it incidentally in a communication made to the Société Chimique in December, 1896, on questions relating to the analysis of phosphates, but I did not lay much stress on the subject.

My attention has been recalled to this matter by a paper by M. Barthe (*Bull. Soc. Chim.*, Series 3, vol. xxiii., p. 422) on the ammonio-earthly phosphates, in which, after

having referred to Kippenberger's statements, and pointed out their errors, he describes a number of negative experiments, and concludes that the only ammonio-magnesian phosphate exists among the alkaline-earthly ones.

I can only confirm the results of these experiments, since we do not easily find the ammonio-calcic phosphate under the conditions arranged by M. Barthe. This body is fairly soluble in, or at least easily decomposed by, water, and the complete insolubility of the tri-calcic phosphate causes the precipitation of the latter, which is obtained by itself as soon as the solution of phosphate of lime is made alkaline by ammonia, no matter what other precautions may be taken.

It is no longer the same, however, if we prevent the precipitation of the tri-calcic phosphate by means of citric acid, and in this case we are able to obtain the ammonio-calcic phosphate.

This is what happens if we treat a solution of phosphate of lime free from magnesia, with citrate of ammonia and ammonia. When the temperature is brought down to about 6° we obtain fairly large and brilliant crystals which consist of ammonio-calcic phosphate. It is in this manner that I obtained this body for the first time, by accident, while trying to determine whether the magnesia could be estimated in a phosphate by direct precipitation.

In the crystals obtained I was able to detect the presence of ammonia, and after calcination I found:—

Lime	0.1882
Phosphoric acid.. .. .	0.2265

which is in theoretical proportion.

Further, in the uncertainty in which I was at this time as to the exact nature of the body obtained, I weighed the lime in the form of carbonate and of sulphate for the purpose of verifying its identity, and I found:—

Carbonic acid	0.1482
Sulphuric acid	0.2660

which represents the correct equivalent of these acids for the above mentioned quantity of lime found.

I have recently repeated these experiments, taking an excess of pure carbonate of lime dissolved in hydrochloric acid and pure phosphate of ammonia. This mixture was treated with a quantity of citrate of ammonia sufficient to keep the phosphate of lime in solution in a strongly ammoniacal solution. The solution was exposed to a temperature of about 4° to 6°, during the night, and hard, transparent crystals were obtained of a size easily discernible by the naked eye.

In this first attempt I did not dare to wash these crystals thoroughly for fear of seeing them disappear, as I was already aware of their easy decomposition, and, for the same reason, I simply pressed them between sheets of blotting-paper after a slight washing with water containing one-third ammonia before proceeding with their analysis.

In a second experiment I slightly increased the quantity of phosphate of ammonia, and made the solution much more ammoniacal in the hope of obtaining an increased return, but under these conditions nothing but triammonic phosphate was separated, almost free from lime. The very slight solubility of the triammonic phosphate in the ammonia concentrated to half the total volume is a danger which must be guarded against.

To obtain larger quantities of the product it is advisable to dissolve 10 grms. of pure carbonate of lime in hydrochloric acid, then add citric acid so that the ammonia will not give any precipitate in the presence of phosphoric acid. About 15 grms. of citric acid are required for each gramme of lime.

To this solution, made slightly alkaline with ammonia, we add every day a little phosphate of ammonia in concentrated solution, and ammonia, and leave the whole each night where the temperature will fall to about 6°.

These progressive additions enable us to obtain a sufficient quantity of the ammonio calcic phosphate to carry

out a proper examination, by almost completely avoiding the separation of the triammonic phosphate; wash with water containing one-third of ammonia, then drain and leave the crystals in the desiccator for two or three days.

The products obtained in the first experiment and in the last have been analysed. The phosphoric acid was weighed as pyrophosphate of magnesia, after precipitation by ammoniacal chloride of magnesium in the presence of citrate of ammonia and ammonia in excess; the lime was estimated in the form of sulphate separated by alcohol, and the ammonia by distillation. The loss at 100° was also estimated as well as the loss by calcination before the blowpipe. These analyses led to the formula $\text{PO}_4\text{Ca}.\text{NH}_4.7\text{H}_2\text{O}$.

The following are the results compared together:—

	Theory.	I.	II.
Phosphoric acid..	25'45	25'50	26'09
Lime	20'07	19'09	19'79
Loss at red-heat ..	54'48	55'24	54'01
	100'00	99'83	99'89
Nitrogen	5'02	6'98	5'30
Loss at 100°	—	48'27	47'96

We thus found an excess of phosphoric acid and nitrogen easily explained by what has been observed with regard to the almost complete insolubility of the triammonic phosphate—an excess which is more noticeable in No. 1, as this sample was only slightly washed and contained ammoniacal water held in the interstices. The variations being much less with No. 2, which was more thoroughly washed and dried, it is safe to admit that if the washing with ammoniacal water and the drying were better done we should get at the composition with greater accuracy.

It is easy, in fact, to calculate that these products contain:—

	I.	II.
Ammonio-calcic phosphate ..	95'02	98'60
Triammonic phosphate..	2'62	—
Biammonic phosphate	—	1'40
Ammoniacal water	2'34	—
	100'00	100'00

During the long time No. 2 was in the desiccator the triammonic phosphate, which was still present, was partially decomposed.

The loss at 100° shows that at and above this temperature partial dissociation and loss of ammonia takes place; for the loss of $7\text{H}_2\text{O}$ would only give 45'17 per cent.

When left to the temperature of the laboratory in a loosely stoppered flask the product effloresced and lost water slowly. The loss amounted to 6'28 per cent in six weeks.

Dissociation by Water.

Experiment 1.—One grm. of the material was ground up with 100 c.c. of water, and left to digest for three-quarters of an hour. A slightly ammoniacal reaction was observed in the atmosphere of the flask, though it was only detected with difficulty. The solution was filtered with a view to titrating the phosphoric acid separately in the solution and in the precipitate. This latter had become amorphous, but there was always a trace of crystalline material left.

Experiment 2.—This was conducted in the same manner except that the mixture was boiled for three-quarters of an hour. The evolution of ammonia was distinct, and the precipitate entirely amorphous. The solution was filtered, and the solution and precipitate were analysed separately. The following are the results:—

	I.	II.
Phosphoric acid, { In solution ..	7'99	9'62
per cent . . { Insoluble ..	18'07	16'44
	26'06	26'06

We see that the product is dissociated by cold water, and if we remember that in No. 1 there was still a little of the crystalline material left, we must admit that the decomposition under these conditions is fairly rapid without being instantaneous, and gives both tricalcic phosphate and triammonic phosphate.

When heated, secondary reactions take place and complicate the results.

Although ammonia is given off, very little it is true, more phosphoric acid goes into solution than there should by simple decomposition. There is a double tendency; that of the ammonia to form biammonic phosphate, and that of the lime to become transformed in the alkaline solution into products containing more lime than the tricalcic phosphate.

In no case and at no moment is the least trace of lime found in solution; this, however, was easy to foresee. If the ammonio-calcic phosphate is soluble it is virtually in this sense that the decomposition is instantaneous.

Practically it is only retarded by cohesion. It is thus proved that an ammonio-calcic phosphate really exists, only differing from the ammonio-magnesian phosphate by the amount of water of crystallisation.

I have not yet succeeded in obtaining the ammonio-barytic phosphate by the same method; in dilute solution nothing is obtained, and if the solution is concentrated it is the triammonic phosphate that is first separated.

The ammonio-calcic phosphate being difficult to obtain, as has been shown, it suffices for the solubility or the dissociation of the corresponding baryta compound to be a little greater for the exact conditions of dilution and temperature to be still more difficult to fulfil.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 5.

CHLOROBROMIDES OF THALLIUM. COMPOUNDS OF THE TYPE Tl_4X_6 .

By V. THOMAS.

A FAIRLY large number of chlorobromides belonging to this series have been described. They were prepared by means of either one of the following methods:—

1. *The Action of Bromine on Thallous Chloride in the presence of Water.*—MM. Carl Wiegand and Jos. Meyer (Wiegand, Inaug. Dissert., Berlin, 1899; Meyer, *Zeit. für Anorg. Ch.*, 1900, p. 321) obtained a chlorobromide with the formula $\text{Tl}_6\text{Cl}_5\text{Br}_2$, which they regarded as a mixture of TlCl with a new chlorobromide, $\text{Tl}_4\text{Cl}_4\text{Br}_2$.

Mr. Cushman (*Am. Chem. Journ.*, 1900, p. 222) attributed to the body thus formed the formula $\text{Tl}_4\text{Cl}_4\text{Br}_2$.

2. *The Action of the Chloride on Thallous Bromide in the presence of Water.*—MM. Carl Wiegand and Jos. Meyer obtained a compound, $\text{Tl}_4\text{Cl}_2\text{Br}_4$, decomposed by water into a chlorobromide with the formula $\text{Tl}_4\text{Cl}_3\text{Br}_3$.

3. *The Action of TlCl on TlBr_3 in Solution.*—MM. Carl Wiegand and Jos. Meyer obtained $\text{Tl}_4\text{Br}_4\text{Cl}_2$; Mr. Cushman obtained $\text{Tl}_4\text{Cl}_3\text{Br}_3$.

4. *The Action of TlBr on TlCl_3 in Solution.*—According to the German chemists $\text{Tl}_4\text{Cl}_4\text{Br}_2$ is formed, but according to Mr. Cushman, $\text{Tl}_4\text{Cl}_3\text{Br}_3$.

5. *The Decomposition of the Chlorobromides of the Type Tl_2X_4 on contact with Water.*—The chlorobromide, $\text{Tl}_3\text{Cl}_2\text{Br}_4$, obtained by MM. Carl Wiegand and Jos. Meyer, decomposes on contact with boiling water, giving rise to the compound $\text{Tl}_4\text{Cl}_4\text{Br}_2$. The chlorobromide, $\text{Tl}_3\text{Cl}_2\text{Br}_4$, should decompose in a similar manner.

According to these researches it would appear that there exist three chlorobromides of the type Tl_4X_6 , corresponding respectively to the formulæ, $\text{Tl}_4\text{Cl}_4\text{Br}_2$, $\text{Tl}_4\text{Cl}_2\text{Br}_4$, and $\text{Tl}_4\text{Cl}_3\text{Br}_3$.

* According to this writer the compound obtained should be isomeric with that formed from $\text{TlCl} + \text{TlBr}_3$.

In the course of my researches I have always obtained a well-defined chlorobromide, $Tl_4Cl_3Br_3$. This in certain cases was mixed with a very small quantity of a chlorobromide having the formula $Tl_4Cl_4Br_2$. These researches were directed principally to the examination of the raw product resulting from the action of bromine on thallous chloride.

The action of bromine in small quantities on thallous chloride in the cold and in contact with water gives a yellow powder of which the composition is not constant, and depends on the quantity of bromine added. Its composition appears to oscillate between the limits $TlCl$ at $Tl_4Cl_3Br_3$.

The raw product dissolved in water crystallises in flakes mixed with a certain quantity of needles, and the first deposits are always of the same composition, viz., $Tl_4Cl_3Br_3$. It is exactly the same if we add bromine to a warm concentrated solution of thallous chloride. The flakes are produced immediately, or on cooling, and correspond to the formula $Tl_4Cl_3Br_3$.

In the first series of experiments the following method of working was adopted:—9.6 grms. of thallous chloride were rubbed up with a little water (50 c.c. or 100 c.c. for example), then 2 grms. of bromine were added; that is to say, a quantity slightly superior to the amount theoretically necessary to transform the $TlCl$ into a compound of the type Tl_4X_6 (the theoretical quantity is 1.6 grms.).

In this manner, when all the bromine had disappeared, we obtained a yellow powder insoluble in the cold. A large quantity of water was added to make the total bulk about a litre; this was then boiled until everything soluble had gone into solution.

During the heating a slight hydrolysis was observed. The solution was filtered so as to have a perfectly clear liquid, and was then submitted to fractional crystallisations.

On submitting the solution to a very slow cooling we observed at about 40° a deposit of small hexagonal flakes. When the temperature reached 33° the product formed was collected, and its weight was almost 2 grms. (product No. 1). Between 33° and 24° (the temperature of the laboratory in which the experiments were carried out) we obtained a fresh deposit exactly similar in appearance to the first one and of about the same weight (product No. 2).

The solution was then concentrated, and its concentration was such that on cooling about 3 grms. of a product were obtained, distinctly different from the others in that it was not homogeneous (product No. 3). It consisted to a great extent of very well formed needles, often grouped together in fern-like clusters. These needles were mixed with hexagonal flakes analogous to those of the preceding deposits.

Further, all these products have a more or less deep orange colour; the needles have the greatest depth of colour.

If we continue to concentrate the mother-liquor we obtain hexagonal flakes (product No. 4); then when the concentration is pushed further we obtain a fresh crop of needles.

Up to the present we have not succeeded in preparing these needles directly in a state of absolute purity.

The conditions under which they can be prepared, independently of the hexagonal flakes, are not yet known.

Two facts only ought to be considered as being well proved; that is to say, the influence exercised on the formation of this body by the concentration of the solution on the one hand, and by the rate of cooling on the other.

To observe its formation it appeared to be necessary to operate on concentrated solutions and to avoid rapid cooling.

The following results of analysis are those of the different products obtained from the same preparation. The estimations of the total halogens and the separation of the chlorine and bromine were made on different portions:—

	AgCl+nAgBr.	Cl.	Br.	Tl (thallous).
<i>Product No. 1.</i>				
Homogeneous. Orange coloured hexagonal plates	84.51 84.13	8.96	20.58	52.35
<i>Product No. 2.</i>				
Homogeneous. Orange coloured hexagonal plates	84.51 85.03	8.75	20.90	52.53
<i>Product No. 3.</i>				
Needles mixed with hexagonal plates ..	84.92 83.13 84.46	10.79	17.34	—
<i>Product No. 4.</i>				
Orange yellow hexagonal plates	84.20	11.52	16.15	—

Whatever the preparations may be these figures are constant. The analysis of compounds corresponding to those in the first two horizontal lines, but coming from different preparations, gave $AgCl+nAgBr$, 86.91 and 84.93, 84.46 and 84.85, 85.30 and 84.84; Cl , 8.94, 8.84, and 9.13; Br , 20.44, 20.53, and 20.70.

For the non-homogeneous products mentioned in the two last lines the figures found by analysis were:— $AgCl+nAgBr$, 84.60, 84.13, and 84.53; Cl , 10.40 and 10.07; Br , 17.77 and 18.88.

These analytical results are all very interesting. They show distinctly that under the conditions of the experiment:—

1. The first deposits have always the same composition, and correspond exactly with the formula $Tl_4Cl_3Br_3$, which requires $AgCl+nAgBr$, 85.54; Cl , 9.15; Br , 20.65.

2. The proportion of bromine is lowered, and that of the chlorine increased at the same time that the needles appear.

3. The deposits which form after the appearance of the first needles, even when they consist entirely of hexagonal plates, are distinguished from the preceding deposits by a smaller proportion of bromine and a higher proportion of chlorine.

Under these conditions there still remains a very important point to elucidate. Have the needles which are formed at the same time as the plates the same composition as these latter, or do they correspond to a different atomic ratio between the thallium, the chlorine, and the bromine?

With a view to solving this problem we felt constrained to operate on a much greater quantity of thallous chloride as the original material, and to separate out the needles formed one by one.

For this purpose we took the following weights:— $TlCl$, 36 grms.; Br , 3 c.c.; water 2 litres.

The deposit obtained was treated with boiling water, and the solution left to itself in a suitable place to avoid any rapid fall of temperature. The crystals deposited were picked out and collected one by one with the help of a low power lens; then, as the needles often had small hexagonal plates attached to their sides, they were again gone over, and picked out with the help of a stronger lens, or even, if necessary, a microscope. In a week a sufficient quantity was collected to enable several analyses to be made.

These left no doubt as to the nature of the product, which corresponded to the formula $Tl_4Cl_4Br_2$.

Analysis.—Found, $AgCl+nAgBr$, 84.65 and 85.96; Cl , 13.32; Br , 14.53. Calculated for $Tl_4Cl_4Br_2$: $AgCl+nAgBr$, 84.97; Cl , 12.70; Br , 14.31.

The plates and the needles* appeared to belong to the

* In a note published in the *Comptes Rendus*, November 4, 1901, we gave this body the formula $Tl_4Cl_3Br_3$ through a mistake which occurred in calculating the formulae $Tl_4Cl_3Br_3$ and $Tl_4Cl_4Br_2$; we take this opportunity of making this correction as our analyses were not published. This formula agrees very well with the note which appeared in the *Comptes Rendus*, of November 26, 1900. They are contradictory with regard to those in my paper of January 14, 1901.

same crystalline system, but we could not be certain on this point without obtaining measurable crystals, and making the usual measurements.

We can pass, however, very easily from plates to needles, and from needles back to plates. The experiment can be repeated indefinitely by taking a hot saturated solution either at a constant or a variable temperature.

This phenomenon shows us distinctly how complex are the conditions of equilibrium which affect the formation of such and such a chlorobromide.

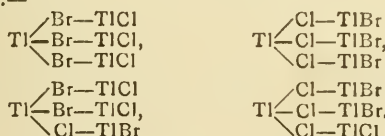
It is especially the chlorobromide, $Tl_4Cl_3Br_2$, which is formed by the decomposition of the $Tl_3Cl_2Br_4$, and obtaining the needles $Tl_4Cl_3Br_2$ is extremely interesting, as this body would represent the hypothetical chlorobromide which Wiegand prepared mixed with $TlCl$, the mixture having the rough formula $Tl_5Cl_5Br_2$. It should also be identical with the plates $Tl_4Cl_3Br_2$ prepared by Cushman.

Both needles and plates have exactly the same properties. Under the action of heat, either when heated directly or when heated in the solution from which they are deposited, they undergo a remarkable change of colour. When hot they take a blood-red colour; this phenomenon is, in fact, produced with a very slight elevation of temperature.

Towards 35° the original colour changes in a very distinct manner. This red colouration disappears more or less rapidly on cooling, and gives place to the original orange colour. When heated in Maquenne's apparatus the two chlorobromides attack the copper and fuse at about 240° .

The chlorobromides of the type Tl_4X_6 are also of great interest from the theoretical point of view. Werner's theory, like that of Blomstrand-Jørgensen on the constitution of double salts, enables us to predict two isomeric derivatives for such compounds.

We might have, for example, according to the Blomstrand-Jørgensen theory, the following compounds as isomers:—



By Werner's hypothesis we ought to admit an atom of Tl placed in the centre of an octahedron, and the two salts in question would become stereo-isomers according to the position of the atoms TlX_6 .

According to Cushman, these two theoretical stereo-isomers would correspond in practice to different substances. This writer claims to have obtained, under the following circumstances, the isomers of the formula $Tl_2Cl_3Br_2$:—

When thallous bromide, in suspension in warm water, is treated with a dilute solution of thallic chloride an orange-coloured compound is obtained; on dissolving, by boiling the solution and then re-cooling, orange-coloured hexagonal plates are deposited. For the sake of brevity we will call this compound α .

On the other hand, if thallous chloride is suspended in a considerable quantity of warm water and treated with a warm concentrated solution of thallic bromide, a blood-red compound is produced which, on re-dissolving by heat and then rapidly re-cooling the solution, gives a deposit of blood-red hexagonal crystals; we will call this product β .

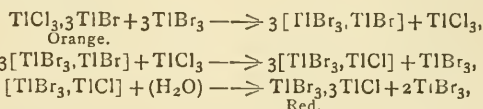
Now, according to Mr. Cushman, the derivatives α and β are isomeric. The derivative α is stable; the derivative β , on the other hand, seems to be characterised by its instability.

We have not repeated these experiments, as the details for carrying them out are entirely wanting.

In any case it is probable that the existence of a few needles in the plates submitted to analysis does not exercise any great influence on the proportion of chlorine; in fact, for $Tl_4Cl_3Br_2$ we ought to have $Cl, 9.15$; and for $Tl_4Cl_4Br_2$, $Cl, 12.70$.

At the same time we were surprised that the facts observed by us had not been noticed as much as those published by MM. Wiegand and Jos. Meyer and Mr. Cushman. In no paper have we found any mention of needles of the composition $Tl_4Cl_3Br_2$, and in no paper is the change of colour which is so characteristic of the compounds of the type Tl_4X_6 mentioned.

We cannot, however, admit that the so-called stereo-isomers of Mr. Cushman are identical with the compounds $Tl_4Cl_3Br_3$ (orange and red modifications) that we have previously described; all we have been able to find in his work seems, on the contrary, to show a deep division between the two series of bodies. The derivative β (red derivative) appears only to be obtained in the presence of an excess of thallic bromide, and the derivative α in the presence of an excess of thallic chloride. We could easily pass from one form to the other according to the equations:—



This question of isomerism should be proceeded with cautiously, and we have no doubt but that Mr. Cushman while continuing his researches will eventually be able to throw greater light on the results of his earlier work.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 11.

THE PRECIPITATION AND SEPARATION OF SILVER IN THE ELECTROLYTIC WAY.*

By W. H. FULWEILER and EDGAR F. SMITH.

THE fact that silver can be quantitatively determined in the electrolytic way is well known. It has had ample confirmation in this laboratory, where numerous estimations of the metal in cyanide solution have been made. It is probable, too, that it was here that the first quantitative results with this electrolyte were obtained, although it is customary to credit the method to Luckow, notwithstanding, in his published account of the electro-deposition of silver from its double cyanide solution, he presents no quantitative data, and merely remarks in regard to such solutions:—"So fällt aus solchen Lösungen das Silber gleichmässig in regulinischer form mit mattem Metallglanze nieder" (*Zeit. Anal. Chem.*, xix., 15). But, be that as it may, without any further reference to the origin of the method, the latter is most deserving of consideration, and to extend in some measure its general applicability we have made separations of silver from solutions in which three or four other metals were simultaneously present. It is the results in this direction which we most desire to put upon record.

Those interested in electro-chemistry will at once recall that in the hundreds of separations made with the current more than two metals rarely were present in the electrolyte. Now that electro-chemical analysis is daily becoming more prominent, the proper working conditions for such problems should be ascertained. It is probable that this phase in electrolysis has been too long neglected. We give first results obtained with silver alone (Table I.).

In trials 1 and 2 the metal was precipitated upon a dish, while in 3 and 4 a plate cathode, and in 5 and 6 a cone was used to receive the silver, which was very adherent and brilliant in lustre. It was washed with water, alcohol, and ether.

Silver from Copper.

The first thought was to further test the separation of silver from copper, making a special point in varying the quantity of the latter metal (Table II., A).

* Contribution from the John Harrison Laboratory of Chemistry, from the *Journal of the American Chemical Society*, xliii., No. 8.

TABLE I.

	Silver. Grm.	Dilution. C. c.	Potassium cyanide. Grms.	Current. N. D. ₁₀₀ .	Volts.	Temperature.	Time. Hours.	Silver found. Grm.
1	0.2133	125	2	0.03 A	2.5	65°	4	0.2132
2	0.2133	125	2	0.03 A	2.5	60°	3	0.2133
3	0.2133	125	4	0.04 A	2.5	60°	3	0.2131
4	0.2133	125	2	0.025 A	2.7	60°	4	0.2134
5	0.2133	125	2	0.025 A	2.7	60°	3	0.2135
6	0.2133	125	2	0.025 A	2.7	60°	4	0.2125

TABLE II.—Silver from Copper.

Silver. Grm.	Copper. Grm.	Potassium cyanide. Grms.	Dilution. C. c.	Current. N. D. ₁₀₀ .	Volts.	Temperature.	Time. Hours.	Silver found. Grm.
A.								
0.1066	0.1053	2	125	0.021 A	1.2	60°	4½	0.1066
0.1066	0.1053	2	125	0.02 A	1.25	55°	6	0.1064
0.1066	0.1053	2	125	0.02 A	1.25	55°	6	0.1065
B.								
0.1066	0.2106	2	125	0.02 A	1.25	60°	3½	0.1066
0.1066	0.2106	2	125	0.02 A	1.25	65°	3½	0.1065
C.								
0.1066	0.5265	4	125	0.03 A	1.2	65°	3½	0.1066
0.1066	0.5265	4	125	0.02 A	1.2	60°	3½	0.1068

TABLE III.—Silver from Copper and Cadmium.

Silver present. Grm.	Copper present. Grm.	Cadmium present. Grm.	Potassium cyanide. Grms.	Dilution. C.c.	Current. N.D. ₁₀₀ .	Volts.	Temperature.	Time. Hours.	Silver found. Grm.	
A.										
0.1066	0.1053	0.1128	3	125	0.02 A	1.25	65°	3½	0.1063.	
0.1066	0.1053	0.1128	3	125	0.015 A	1.25	65°	4	0.1069	
0.1090	0.1053	0.1128	3	125	0.02 A	1.25	65°	4	0.1090	
B.										
Zinc present. Grm.										
0.1090	0.1053	0.1128	0.1244	4	125	0.02 A	1.25	80°	5	0.1092
0.1090	0.0526	0.0564	0.0622	5	125	0.02 A	1.25	75°	6	0.1089
0.1090	0.0526	0.0564	0.0622	3.5	125	0.02 A	1.25	75°	5	0.1087

TABLE IV.—Silver from Copper, Cadmium, Zinc, and Nickel.

Silver. Grm.	Copper. Grm.	Cadmium. Grm.	Zinc. Grm.	Nickel. Grm.	Potassium cyanide. Grms.	Dilution. C. c.	Current. N.D. ₁₀₀ .	Volts.	Temper- ature.	Time. Hours.	Silver found. Grm.
0.1090	0.0526	0.0564	0.0622	0.0411	4.5	125	0.02 A	1.2	75°	5½	0.1086
0.1090	0.0526	0.0564	0.0622	0.0411	3.5	125	0.02 A	1.2	75°	5	0.1085

The silver was completely precipitated. It was found to be free from copper.

The next ratio was 1Ag:2Cu (Table II., B).

With the ratio 1Ag:5Cu the results were as given in Table II., C.

The experience gathered from these determinations shows that the separation of these two metals can be conducted in this particular way with the certainty of success. In several instances the liquid from the silver was diluted to 500 c.c. and electrolysed with a more powerful current when the copper was fully precipitated, and showed the absence of silver upon applying the customary tests.

Silver from Copper and Cadmium.

(See Table III., A).

The next step was the introduction of a zinc salt into the electrolyte. Strangely enough some cadmium was now found in the deposit of silver, but it was not long before the observation was made that if the electrolyte was heated to 75–80° before passing the current the co-precipitation of cadmium could be absolutely prevented. The conditions are indicated in Table III., B.

The silver was found free from any of the other metals. In all the experiments made with the conditions as re-

corded in the preceding paragraphs, the striking brilliant lustre of the deposited silver was particularly marked.

Silver from Copper, Cadmium, Zinc, and Nickel.

(See Table IV.).

None of the other metals were found in the silver deposit. The addition of the nickel to the solution seems to retard the precipitation of silver to a slight degree.

A Method for Detecting Free Phosphorus.—P. Muckerji.—The material in which it is sought to detect free phosphorus is placed in a hydrogen generator ($\text{SO}_4\text{H}_2 + \text{Zn}$), giving an abundant flow of gas at a temperature of 60–70°; the apparatus is placed in the dark, and we notice whether the unlighted gas emits any light. This method is at least as sensitive as that of Mitscherlich. Phosphites and hypophosphites, and phosphides of hydrogen do not give any phosphorescence. The substances which interfere with the phosphorescence of phosphorus in the air under ordinary conditions have their influence diminished in this case. When the operation is finished it is necessary to displace the gas by filling the apparatus with water to prevent spontaneous combustion.—*Zeit. Anorg. Ch.*, vol. xxvii., p. 72.

NOTICES OF BOOKS.

Twenty-sixth Annual Report of His Majesty's Inspectors of Explosives; being their Annual Report for the Year 1901. London: Eyre and Spottiswoode. Edinburgh: Oliver and Boyd. Dublin: E. Ponsonby. 1902. Pp. 230.

THE only modifications of the law made during the past year have been two Orders of Secretary of State of limited application, which will be found in Appendices F (1) and F (2). The former of these deals with the packing of electric detonators, and the latter grants an exemption for acetylene, when compressed into certain porous substances, from being a prohibited explosive.

The growth of trade in explosives has continued during the early part of the past year, but there have been some signs that during the latter half of the year the rate of increase was not sustained.

We are glad to note that as a result of the inspectors' visits to the various factories and magazines throughout the kingdom there is no reason to complain that there is any falling off in their condition or management. Occasions when such serious irregularities are found as to necessitate legal proceedings are now rare. The number of deaths (ten) from accidents by fire or explosion in the manufacture of explosives is unfortunately above the average for the decade (5.4), but this number of deaths is not excessive, and will compare favourably with the death-rate in other dangerous trades.

The total number of factories under continuing certificate or license is 150. This does not include "small firework" or "toy firework" factories. Of the above total number, four factories are under notice of temporary disuse. The total number of factories which have come into existence since the commencement of the Act has been 150, but 55 have become extinct, so the net increase is 95; for the present year there is no increase.

There have been twenty articles added to the authorised list of explosives, and two removed.

During the year, 249 visits have been paid to factories, but in very few cases had proceedings to be taken.

The number of accidents in factories is 76, causing 10 deaths and injuring 38 persons. These accidents are dealt with in detail, but a considerable proportion of them are of an unimportant character, such as the fuming off of gun-cotton in the acid centrifugals, while some of the injuries were only slight.

There are now 393 magazines under continuing certificate and license, being an increase of 8 on the number for 1900, and these have been visited 462 times; in very few instances were serious defects or irregularities found, and, in general, the condition of magazines throughout the country is highly satisfactory. No legal proceedings have been taken throughout the year.

The amount of foreign nitro-glycerin compounds imported in 1901 is 1,473,950 lbs., against 998,030 lbs. in 1900; there has also been an increase in the importation of blasting explosives not containing nitro-glycerin from 129,750 lbs. in 1900 to 142,900 in 1901.

With regard to the chemical work of the department, conducted by Dr. Dupré, F.R.S., 427 articles have been examined; this is a slight decrease as compared with the previous year. These articles are divided into three classes:—

1. Samples of licensed explosives and materials used in the manufacture of such explosives.
2. Articles which do not properly come under the above heads.
3. All explosives examined in connection with the Woolwich testing station.

Of the first class, 335 were passed and 44 rejected; the somewhat larger number under the heading of "rejected" is mainly due to the fact that owing to requirements under the Mines Act, the compositions of explosives permitted to be used are fixed more closely than in former years. Much

work has been done in order to keep analytical methods fairly abreast of requirements. The compositions of explosives generally are becoming more complicated, and the limits within which variations are allowed are being drawn more and more narrowly; the correct analysis of explosives thus becomes increasingly difficult. Some explosives contain as many as eight constituents, and their correct analysis is often a matter of some difficulty.

A number of accidents and explosions abroad are described and commented upon, and the report closes with the usual appendices giving full details of the various matters referred to in the body of the report.

La Grande Industrie Chimique Minérale. ("The Industries of Mineral Chemistry"). By E. SOREL. Paris: C. Naud. 1902.

THIS treatise differs in some respects from the ordinary run of books on industrial chemistry. In many instances it must be supplemented by reference to books on general chemistry for details concerning the characteristic properties of the substances considered. On the other hand, the author's wide experience eminently fits him to produce a comprehensive and complete work of reference for the use of the manufacturer. Nearly half the volume is occupied by the study of sulphur and its derivatives, the manufacture of sulphuric acid naturally receiving special attention. This part is well balanced and exact, and should commend itself to the student of chemical industries. Under nitrogen are included nitrates and nitric acid, ammoniacal salts, and compounds of cyanogen. The third part is devoted to the phosphates, treated both from an agricultural and industrial point of view. Here the treatment is occasionally not altogether satisfactory, as, for instance, in the case of the phosphoric acids; and some omissions may be noticed. In fact, the end of the book hardly reaches the same standard of excellence as the beginning, and signs of less careful writing may be detected. The last part includes the alums and vitriols of iron, copper, and zinc. The usefulness of the book is seriously impaired by the absence of an alphabetical index.

Rapports du Jury International de l'Exposition Universelle de 1900. Classe 90. Parfumerie. ("Reports of the International Jury of the Paris Exhibition. Class 90. Perfumery"). By L. V. PIVET. Paris: Imprimerie Nationale. 1901.

THIS report of the international jury on the perfumery class of the Paris Exhibition forms a concise and useful account of the subject. The historical chapters include tables illustrating the state of the French export trade in essences and perfumes generally. The second of the five parts into which the book is divided treats of the rôle played by science in the industries; in an introductory chapter on the constitution and physiology of odorous bodies, theoretical considerations are shortly reviewed; the chapter on the chemical constituents of essences gives physical and other data concerning various substances of importance in perfumery; unfortunately, however, the information is not always accurate; for instance, a CH group is omitted in the formula of cinnamic aldehyde, which is written $C_6H_5-CH=COH$, and the boiling-point of the same substance is incorrectly given. The methods of analysis of the natural products, essential oils, and essences, and the state of the industry at the present time in various countries, occupy the third and fourth parts; the latter includes tables of exportation from, and importation into, France for the year 1900, and the volume ends with a list of awards in this and previous Exhibitions. The study of the subject of perfumery is one which requires a considerable knowledge of chemistry, and the employment of methods based on scientific foundations should tend to increase and develop the trade; this book, quite

apart from its reference to the Exhibition, appears to be a useful little handbook and compilation.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by FRANZ HOFMEISTER. Band II. 5 and 6 Heft. Braunschweig: Friedrich Viewig und Sohn. 1902.

THE May number of this journal opens with a paper by Dr. Paul Mayer, describing his researches on the formation of indoxyl, phenol, and glycuronic acid, in cases of phloridzin diabetes; the author believes that he has established the fact that no increase takes place in the formation of any of these substances, a conclusion which does not agree with Lewin's results published some months ago in an earlier number of the journal. C. Neuberg and F. Blumenthal contribute a paper on the formation of iso-valeric acid and acetone by the oxidation of gelatin; and much interest attaches to a communication by Dr. P. Bielfeld on the subject of the iron contained in human liver cells. The question of the origin of the various compounds of iron known to occur in the liver is not discussed, but the results of many careful and exact determinations of the iron in normal liver cells are given, with a view to determining in which sex and at what age, generally speaking, maxima of percentages of iron are reached. The systematic examination of these and similar details should help to add to our at present scanty knowledge concerning the connection between the simple and complex iron salts found in the human liver.

CORRESPONDENCE.

THE MELTING-POINT OF CHROMIUM.

To the Editor of the Chemical News.

SIR,—In my recent note on "The Melting-point of Chromium" (CHEMICAL NEWS, vol. lxxxvii., p. 13), I stated that the chromium contained 99 per cent of chromium; this was the approximate amount the makers said it contained. An analysis of it gave—

Aluminium	traces
Iron	1·23 per cent
Silicon	0·14 "
Chromium	98·63 "
	100·00 "

Mr. Hogg, in his letter (p. 35), says that aluminium is "reputed to lower the melting-point of certain metals enormously." This is a mistake, as small percentages of aluminium do not lower the melting-points of metals to the extent it was at one time supposed. In the "Third Report to the Alloys Research Committee of the Institution of Mechanical Engineers," Roberts-Austen showed that the addition of 1 per cent of aluminium to pure iron did not lower the melting-point much below the melting-point of pure iron; and I do not see why, even if it was present to the extent of 1 per cent, it should lower the melting-point of chromium.

In a recent paper (see *Journal of the Society of Chemical Industry*, June 30, 1902) I pointed out that the melting-point of manganese, usually stated to be 1900° C., was only 1280° C., and I thought it would be interesting to determine if chromium had the high melting-point usually attributed to it, namely, considerably over 1775° C.

Mr. Hogg quotes some experiments by Osmond on the melting-point of steel; but it is the carbon which is most probably the cause of the lowering of the melting-point of steel.

I do not claim that my determinations of the melting-point of chromium and manganese are absolutely correct, but I think they will be found to be within 30° C. of the melting-point of the pure metals when they are obtained

chemically pure in sufficient quantity to enable accurate determinations to be made.—I am, &c.,

ERNEST A. LEWIS.

310, Dudley Road, Birmingham,
July 23, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. xxvii., No. 1.

Alloys of Aluminium and Magnesium. — O. Boudouard. — Already noticed.

Action of Fuming Sulphuric Acid on Ethanal, Propanal, and Propanone. — Marcel Delépine. — Trioxymethylene has been shown to react on fuming sulphuric acid, giving a kind of sulphuric acetal of methanal. Similar experiments made with ethanal and propanal have given results of an entirely different character. These aldehydes are sulphonised; the same is the case with acetone. The author then gives the details of a large number of experiments and the analysis of the products obtained.

Synthesis of Dimethylsuccinic Acid under the Influence of Light. — W. Sernow. — If iodopropionic ether is exposed to direct light in the presence of metallic mercury, we observe that the mercury is gradually changed into a reddish crystalline powder of mercuric iodide, and finally the ether contains no more iodine. By shaking up, by means of a motor, 20 grms. of the ethylic ether of α -iodopropionic acid in alcoholic solution with 30 grms. of mercury in a sealed flask in direct sunlight, the reaction is complete in a few sunny days. In this manner the author obtained a product which, when separated with alcohol, took the form of a thick oil. It commences to boil at about 220°, and at 230° the greater part distils over; at 300° and over, decomposition takes place. The 220–230° portion, after several rectifications, boils at 219–220°; its formula is $C_{10}H_{18}O_4$, thus dimethylised succinic ether is formed.

No. 2.

The presence of Tellurium in Ingots of American Silver. — C. Vincent. — Already inserted in full.

Nitromannite and Nitrocellulose. — L. Vignon and F. Gerin. — Already noticed.

Reducing Properties of certain Nitric Ethers. — L. Vignon and F. Gerin. — Already noticed.

Nitric Derivatives of Pentaerythrite. — L. Vignon and F. Gerin. — Already noticed.

Nitrated Derivatives of Arabite and Rhamnite. Constitution of certain Nitric Ethers. — L. Vignon and F. Gerin. — Already noticed.

The Microchemical Detection of Potassium, Rubidium, Cæsium, Indium, and the Hyposulphites. — A. C. Huysse. — The well known precipitates formed by the alkaline salts in the presence of hyposulphite of sodium and bismuth have very characteristic microcrystalline forms. The reagent is prepared by dissolving a little sub nitrate of bismuth in a watch-glass, with the least possible quantity of hydrochloric acid, then adding water until a permanent precipitate is formed, which is re-dissolved in hyposulphite of soda. This solution is treated with alcohol until it commences to appear cloudy, and is clarified by adding a drop of water. The advantage of this method is that ammoniacal salts give no precipitate with the reagent. Hyposulphite of sodium, on the other hand, forms with thalious nitrate a microcrystalline precipitate, which may be used in the absence of the halogen salts. — *Zeit. Anal. Ch.*, vol. xxxix., p. 9.

THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2228.

ON THE ATOMIC WEIGHT OF RADIUM.

By M^{mes}. CURIE.

By concentrating by fractional crystallisation the greater part of the radiferous barium at my disposal I have succeeded in obtaining about 1 decigram of perfectly pure radium chloride. This has enabled me to determine the atomic weight of radium.

It results from the following experiments that the atomic weight of radium is 225 (taking Cl = 35.4 and Ag = 107.8) with a probable uncertainty of not more than one unit, radium being considered a bivalent element.

The method employed consists in estimating, in the state of chloride of silver, the chlorine contained in a known weight of anhydrous radium chloride. As a control experiment I determined the atomic weight of barium by the same method, under the same conditions, and with the same quantity of material. The numbers found always fell between 137 and 138. I have also found that this method gives satisfactory results even with a very small quantity of material.

Many determinations were made with radium chloride; after each operation the radium was brought to the state of chloride in the following manner:—The liquid, containing after the estimation radium nitrate and silver nitrate in excess, was mixed with pure hydrochloric acid. The silver chloride was separated by filtration, and the filtrate was evaporated to dryness several times with an excess of pure hydrochloric acid. Experience shows that all the nitric acid may be eliminated in this way.

The weighings were performed on an aperiodic Curie balance in perfect adjustment, and weighing to the twentieth of a m.grm. This direct reading balance permits of very rapid weighings, an essential condition for weighing the anhydrous chlorides of barium and radium, which slowly absorb water in spite of the presence of desiccating agents in the balance. The substance to be weighed is placed in a platinum crucible; this crucible has been in use a long time, and I have verified that its weight does not vary a tenth of a m.grm. in the course of an operation.

The hydrated chloride obtained by crystallisation was heated in an oven to transform it into the anhydrous chloride. Experience shows that when the chloride was kept for some hours at 100° its weight does not alter, even when the temperature rises to 200° and is kept there for some hours. Therefore the anhydrous chloride so obtained constitutes a perfectly definite body. In all the estimations the chloride was dried at 150°.

M. Demarçay has been good enough to examine the spectrum of the radium chloride submitted to analysis, and has given me valuable indications of the degree of purity of the body.

Two series of experiments were made. The first was with a radium chloride which M. Demarçay considered sensibly pure, but in which the spectrum showed still the three principal lines of barium with good intensity. The numbers obtained in four successive operations were the following:—

220.7 223.0 222.8 223.1

I then undertook a new purification, and succeeded in obtaining a product much more pure. M. Demarçay considers that this second product only contains a minimum quantity of barium incapable of influencing appreciably the atomic weight.

Here are the results of three determinations made with this perfectly pure radium:—

225.3 225.8 224.0

The mean of these numbers is 225.0. I think this number is within one unit of the truth.

The silver chloride from the estimations was always radio-active and luminous. I satisfied myself that it had not carried down a ponderable quantity of radium. I have found also that the weight of radium chloride regenerated did not vary in the operations.

The separation of the radium chloride was effected by fractionally crystallising in a hydrochloric solution a radiferous barium chloride which already had been purified carefully. When the concentration of radium becomes of a certain strength the crystals, at first colourless in the mother-liquor, become yellow or rose coloured a few hours after their deposition. This colouration disappears on solution. It appears to be due to the simultaneous presence of barium and radium, for crystals of pure radium chloride do not become coloured. This observation may be useful for following the course of the fractionation.

Pure anhydrous radium chloride is spontaneously luminous.

From its chemical properties radium is an element of the alkaline-earth series, and in this series it is the higher homologue of barium. According to its atomic weight it should be placed in Mendeleeff's table below barium in the alkaline-earth series, and on the line with thorium and uranium.—*Comptes Rendus*, cxxxv., p. 16r, July 21, 1902.

ON THE MEASUREMENT OF TEMPERATURE.*

PART I.—ON THE PRESSURE COEFFICIENTS OF HYDROGEN AND HELIUM AT CONSTANT VOLUME AND AT DIFFERENT INITIAL PRESSURES

PART II.—ON THE VAPOUR PRESSURES OF LIQUID OXYGEN AT TEMPERATURES BELOW ITS BOILING-POINT ON THE CONSTANT VOLUME HYDROGEN AND HELIUM SCALES.

PART III.—ON THE VAPOUR PRESSURES OF LIQUID HYDROGEN AT TEMPERATURES BELOW ITS BOILING-POINT ON THE CONSTANT VOLUME HYDROGEN AND HELIUM SCALES.

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Part I.—By M. W. TRAVERS and A. JAQUEROD.

PRESSURE COEFFICIENTS OF HYDROGEN AND HELIUM.

THE pressure coefficients have been determined by measuring the pressures which the gases exert when the bulb of the thermometer is in melting ice, or in steam at the boiling-point. Full details of the method employed are given in the paper of which this is an abstract.

The principal new features of the method are as follows:—The gases were introduced into a glass bulb sealed to a capillary glass stem, which was in turn sealed at the other end to the tube which formed the "dead space"; thus eliminating any chance of leakage of the gas, which must necessarily occur when steel tubes, connected to the glass by cement, are employed. The mercury in the dead space was brought close to, but not into contact with, a point in the dead space, and the pressure on the gas in the thermometer was directly observed by measuring the height of the mercury in an exhausted manometer tube above the mercury in the dead space; the apparatus was so arranged that the two mercury menisci lay on the same vertical axis.

The mercury column and the dead space were enclosed between two parallel glass plates in a water-jacket, the temperature of which could be maintained constant, by means of a rapid current of water, to within 0.02° C. In-

* Abstract of a Paper read before the Royal Society, June 19, 1902.

equalities in the temperature of the mercury column and dead space, to which the largest errors in such measurements are due, were thus eliminated.

The scale which formed the first surface of the water-jacket was certainly correct to 0.01 m.m. The distances between the surfaces of the mercury menisci and the nearest division of the scale were measured by means of a telescope with an ocular micrometer placed at a distance of one metre from the apparatus. By this means it was possible to obtain readings concordant to 0.01 m.m.

In calculating the pressure, corrections were made for capillarity, taking into consideration the height of each meniscus, which was measured at each observation, and for the temperature of the column. The volume of the dead space, which varied with the distance of the mercury in it from the point, and with the height of the meniscus, and the expansion of the bulb with the change of temperature and pressure between 0° and 100° C., were taken into consideration in making the final calculations.

In determining the value of the coefficients, the pressures P_0 and P_{100} which the gas would exert, supposing the whole of it was at the temperature of melting ice or of saturated steam under normal pressure, we first calculated. Each of the values of P_0 or of P_{100} given in the following table, is the result of four consecutive measurements of the pressure, temperature, &c.

Pressure Coefficient of Hydrogen.

Series I. (a)	P_0	694.458, 694.452
	P_{100}	948.789, 948.824, 941.809
	α	0.00366261
(b)	P_0	696.103, 666.102
	P_{100}	951.059, 951.044
	α	0.00366252
(c)	P_0	706.528
	P_{100}	965.291
	α	0.00366246
Series II.	P_0	520.326, 520.311
	P_{100}	710.897, 710.882, 710.907
	α	0.00366268

Pressure Coefficient of Helium.

Series I. (a)	P_0	690.232, 690.238
	P_{100}	743.044, 943.044, 942.992
	α	0.00366241
(b)	P_0	671.422, 671.418
	P_{100}	917.322, 917.328, 917.352
	α	0.00366270
Series II. (a)	P_0	522.984, 522.984
	P_{100}	714.576, 714.529, 714.577
	α	0.00366313
(b)	P_0	523.016, 523.020
	P_{100}	714.568, 714.583
	α	0.00366255

We have thus three determinations of the pressure coefficient of hydrogen at an initial pressure of 700 m.m., to the third of which, since it is the result of one measurement of P_0 and one of P_{100} , and was only carried out to make certain that our instrument was in good working order before determining the pressure coefficient for helium, we attach less weight than to the remaining values. The results of the two experiments with helium are of equal value, each being the result of two determinations of P_0 and three determinations of P_{100} . The mean values of the pressure coefficient for both hydrogen and helium appear to approach 0.00366255, a number which agrees very closely with the value obtained by Chappuis (0.00366254), and is somewhat lower than that given by Onnes (0.0036627) as his final result, though differing little from one of his three actual measurements (0.0036625).

The values of the coefficients at lower initial pressures do not show the same concordance as those at higher pressure, but they tend to show that at very low pressures the pressure coefficient does not assume a lower limiting value, the reciprocal of which should be the melting-point

of ice on the absolute scale of temperature. That helium and hydrogen have the same pressure coefficient, and that the coefficient is independent of the pressure, suggest that whatever correction may be necessary to reduce temperatures between 0° and 100° C. on the scale of the hydrogen or helium constant-volume thermometer to temperatures on the absolute scale, it must be very small. Further study of the thermodynamic properties of these gases is necessary for the solution of this important problem.

Part II.—By M. W. TRAVERS, G. SENTER, and A. JAQUEROD.

VAPOUR PRESSURES OF LIQUID OXYGEN.

As has been shown in Part I., the coefficients of increase of pressure at constant volume for hydrogen and helium, between 0° and 100° C., have the same value, viz., 0.00366255 or $1/273.03$.

Numerous measurements of the boiling points and vapour pressures of liquid oxygen on the constant volume hydrogen scale have been made by previous investigators. The values obtained differ by two or three degrees, and even the most reliable measurements vary between -182.4° and -182.7° C. In very few cases are any experimental details given in the original papers; in most cases it is even impossible to ascertain what value was taken for the coefficient of expansion of hydrogen. In every case, however, it appears that the measurements were made by immersing the thermometer in a mass of liquid oxygen, and measuring the pressure under which the liquid was evaporating. As is shown in our paper, it is extremely difficult to maintain liquid oxygen in a steady state of ebullition, and unless a rapid current of air or oxygen is passed into the liquid it ceases to boil, and may become superheated to the extent of more than one degree. Further, it is very difficult to obtain a sufficient quantity of pure oxygen for such a measurement.

In our experiments a bulb in which a small quantity of pure oxygen could be liquefied was immersed together with the thermometer bulb in a vacuum-vessel containing liquid air or oxygen, through which a fairly rapid current of air was passed. The bulb containing the pure oxygen communicated with the lower chamber of a barometer, so that the measurements of the vapour pressure were quite independent of the atmospheric pressure, with a mercury pump, and with an apparatus for generating pure oxygen from potassium permanganate. Simultaneous readings of this barometer and of the thermometer, which contained hydrogen or helium, gave the vapour pressures of pure oxygen at temperatures which could be varied between 80° and 90° Abs., according as the vacuum vessel surrounding the thermometer bulb, &c., contained freshly made liquid air or nearly pure oxygen.

Four thermometers were employed in these measurements, the capacities of the bulbs being approximately 90 c.c., 12 c.c., 26 c.c., and 27 c.c. Only one single set of measurements on the hydrogen scale were made with the large thermometer, which was the same instrument as was employed in the determination of the pressure coefficients of the gases, for though it was possible to observe a steady temperature by means of it with a degree of accuracy approaching one part in 20,000, it was found impossible to maintain so large a thermometer bulb at a constant and uniform temperature, without employing very large masses of liquid oxygen. The results obtained by means of this thermometer differ only by 0.1° from the mean of those obtained by means of the three smaller thermometers. The temperatures observed by means of the three smaller thermometers rarely differ by more than 0.03° from the temperature, corresponding to the same pressures, taken from the smooth vapour pressure curve.

The form of the thermometers employed in this research, and in the measurements of the vapour pressures of liquid hydrogen, was practically the same as that described in the previous abstract; full details are given in the paper. The pressure on the gas in the thermometer was

directly observed by means of a manometer attached to the apparatus, and was independent of the atmospheric pressure. The temperature of the dead space and mercury column were determined by means of mercury thermometers, and the mean temperature of the vertical portion of the stem immediately above the bulb was measured by means of an auxiliary gas thermometer, with a cylindrical bulb of the same length as that portion of the stem of which the temperature is uncertain.

The coefficient of expansion of the glass of which the thermometer bulbs were made was determined by measuring the contraction of the inner tube of a vacuum vessel, 1000 m.m. long, when filled with liquid air. The coefficient between 0° and 100° had been found to be 0.0000284; between 0° and -190° it was 0.0000218.

The pure hydrogen and helium employed in the thermometric measurements was prepared by methods which are described in the next paper, Part III., Appendices II. and III.

The results of our measurements show that with constant volume thermometers, in which the pressure at the melting point of ice is about 1000 m.m., the temperatures between 80° and 90° Abs. on the helium scale are 0.1° higher than on the hydrogen scale. Olszewski obtained identical readings on the two thermometers. This may be accounted for by the fact that he employed helium from clèveite which had only been purified by sparking with oxygen, and which possibly contained a trace of argon or other impurity. Our helium was probably quite pure, as it had been passed through a coil cooled to 15° Abs. in liquid hydrogen, and was therefore a more perfect thermometric substance than that employed by Olszewski.

This result is further discussed in the full paper.

The Vapour Pressures of Liquid Oxygen.

Pressures in millimetres.	Temperatures on the hydrogen scale.	Temperatures on the helium scale.
800	90.60°	90.70°
760	90.10	90.20
700	89.33	89.43
600	87.91	88.01
500	86.29	86.39
400	84.39	84.49
300	82.09	82.19
200	79.07	79.17

Part III.—By M. W. TRAVERS and A. JAQUEROD.

VAPOUR PRESSURES OF LIQUID HYDROGEN.

The liquid hydrogen employed in these investigations was obtained by a method devised by one of us two years ago, and described in the *Philosophical Magazine*, 1901, vol. xvii., p. 412. About 400 c.c. of liquid hydrogen was employed in each of the seven sets of experiments, of which the following are the results. After filling the gasometer with hydrogen, and collecting the quantity of liquid air (8 litres) necessary to cool the apparatus, this quantity of liquid hydrogen can be obtained in half-an-hour from the moment at which the operations are commenced. Our experience has shown us that when liquid hydrogen is once obtained, it is much more convenient to manipulate than liquid air. As its latent heat of vaporisation is very high, little loss is entailed through cooling apparatus, previously cooled in liquid air, to its boiling-point. Further, the liquid shows no tendency to become superheated, and boils steadily, even under reduced pressure.

Dewar (*Roy. Soc. Proc.*, Feb., 1901, vol. lxxviii., p. 40) has obtained the following values for the boiling-point of hydrogen on the constant volume hydrogen scale:— -253.03° , -253.37° , -252.81° , -250.35° ; the pressure on the gas at the ice-point being 287 m.m., 270 m.m., 739 m.m., and 127 m.m. respectively. On the scale of a thermometer filled with helium containing 7 per cent of neon, at a pressure corresponding to 728 m.m. of mercury at the ice-point, he found the temperature to

be 252.68° and 252.84° C. In calculating the temperatures on both thermometers he employed Chappuis's coefficient of expansion for hydrogen, 0.00366254.

In our experiments we have employed the three small thermometers which we used to determine the boiling-point and vapour pressures of liquid oxygen. The thermometers were filled with pure hydrogen or helium, obtained by the methods described in Appendices II. and III. to this paper. The small bulb communicating with a manometer, which had in the former experiments contained pure liquid oxygen for the measurement of the vapour pressure, contained, in these experiments, pure hydrogen from palladium. This method of measuring the vapour pressure was essential to the accuracy of the experiments, for it appeared that the vapour pressure of the pure hydrogen, and of the hydrogen in the vacuum vessel surrounding the thermometer, always differed slightly, probably owing to the presence of impurities dissolved in the latter. The agreement between the results obtained with different thermometers, containing different samples of gas, is indicated in the following table:—

Thermometer.	Vapour pressures of liquid hydrogen. M.m.	Temperature.	
		Found.	From smoothed error.
I. <i>Hydrogen Scale.</i>			
A (12 c.c.)	757.2	20.17°	20.21°
B (26 c.c.)	766.6	20.28	20.25
II. <i>Helium Scale.</i>			
A (12 c.c.)	765.0	20.42	20.44
" "	759.2	20.41	20.41
B (26 c.c.)	770.0	20.43	20.46
C (26.7 c.c.)	749.0	20.36	20.36

The vapour pressures of liquid hydrogen were measured on the hydrogen scale between the boiling-point and a pressure of 100 m.m. of mercury, and on the helium scale between the boiling-point and a pressure of 50 m.m., by a method which is described in detail in the full paper. The temperatures on the helium and hydrogen scales were found to differ to a greater extent than at the temperature of liquid oxygen. The difference, as the following table shows, is from 0.19° to 0.21° over the range of temperature investigated. Considering that the critical-point of hydrogen lies about 35° Abs., while that of helium is probably in the neighbourhood of 10° Abs., this difference is not surprising.

The Vapour Pressures of Liquid Hydrogen.

Pressure in millimetres.	Temperatures on the hydrogen scale.	Temperatures on the helium scale.
800	20.41°	20.60°
760	20.22	20.41
700	19.93	20.12
600	19.41	19.61
500	18.82	19.03
400	18.15	18.35
300	17.36	17.57
200	16.37	16.58
100	14.93	15.13
50	—	14.11

Appendix I.—The melting-point of hydrogen was found to be 14.1° on the helium scale; the temperature given by Dewar in 1901 is 16° (*Roy. Soc. Proc.*, vol. lxxviii., p. 360), but an earlier measurement by him gives the melting pressure as 55 m.m. (*Nature*, Sept. 21, 1899). The details of the experiments cannot be entered into in this abstract.

Appendix II.—The pure hydrogen used in our thermometers, &c., was obtained by means of spongy palladium. The method of purifying the gas is given in detail.

Appendix III.—The gas from the Bath wells is not a good source of helium for thermometric purposes, since it contains much neon, and the latter, as we shall presently show, has a considerable vapour pressure at the tempera-

ture of liquid hydrogen, and cannot be completely separated from the helium.

Pure helium is most readily obtained from clèveite gas, which appears to contain only helium, argon, and a trace of krypton. The gas used in our experiments was passed through a glass coil immersed in liquid hydrogen boiling under normal pressure in one case (Thermometer A), and under a pressure of 110 m.m. of mercury in another (Thermometers B and C). This helium was probably very pure.

Appendix IV.—The following values have been obtained for the vapour pressures of solid neon:—

Temperature (helium scale).	Pressure (millimetres).
20.4°	12.8
15.65	2.4

The vapour pressure of the neon did not change after successive portions of it had been allowed to evaporate. This proved that neon is a homogeneous substance.

Appendix V.—From consideration of the periodic relationship between the critical- and boiling-points of the elements of the helium-argon group, it appears probable that the critical-point of helium lies at about 10.5° Abs. and the boiling-point at 6° Abs.; Dewar (*loc. cit.*, p. 364) fixes the former of these points at below 9° or 10°, and the latter at about 5°. In a series of experiments helium was compressed into a tube, one end of which was cooled in liquid or solid hydrogen. At temperatures down to that of solid hydrogen evaporating under a pressure of 5 m.m. of mercury (probably about 13° Abs.), the pressure on the helium was slowly increased to 60 atmospheres. Under all conditions a change of pressure accompanied a change of volume of the gas, and no evidence that liquefaction had taken place could be obtained.

NOTE OF THE
MATHEMATICAL EXPRESSION OF THE
VALENCY LAW OF THE PERIODIC TABLE,
AND THE NECESSITY FOR
ASSUMING THAT THE ELEMENTS OF ITS
FIRST THREE GROUPS ARE POLYVALENT.*

By GEOFFREY MARTIN, B.Sc. (Lond.).

TAKING as abscissæ the group numbers of the elements as they appear in Mendeleeff's table, and as ordinates the degree of valence, mark out points corresponding to the lowest and highest degree of valence that can be exhibited by each separate element at ordinary temperatures. Join these points, and we get the two straight lines, A, B, C and B, D, intersecting at B at right angles.

Let v represent the valency and n the group number; then the equation to the line A, B, C is—

$$v - n = 0,$$

and the equation to B, D is—

$$v + n - 8 = 0.$$

Combining in one equation these two lines, we get—

$$(v - n)(v + n - 8) = 0,$$

or—

$$v^2 - n^2 - 8(v - n) = 0 \dots (1).$$

This last equation is the mathematical expression of the variation of the valency of any one element with its position in the Periodic Table; at least, for elements of moderate atomic weight and at normal temperatures.

For put n in this equation successively equal to 1, 2, 3, . . . 8, and we get for the valencies—

* By a "polyvalent element," I mean an element that can act with several different degrees of valence towards other radicals.

$n=1$		$v=1$ or 7
$n=2$		$v=2$ or 6
$n=3$		$v=3$ or 5
$n=4$		$v=4$ or 4
$n=5$		$v=3$ or 5
$n=6$		$v=2$ or 6
$n=7$		$v=1$ or 7
$n=8$		$v=0$ or 8

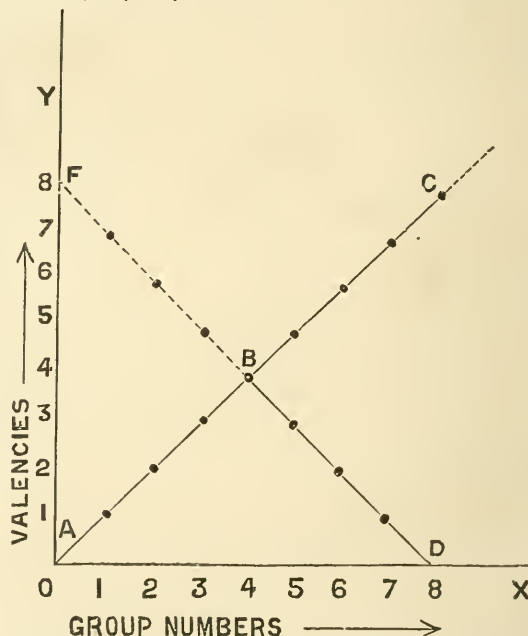
In other words, the degree of valency with which an element can act is—

In Group	Lowest.	Highest.
VIII.	0	8
" VII.	1	7
" VI.	2	6
" V.	3	5
" IV.	4	4

So far, we are merely expressing well known experimental facts; but, assuming the law to be true for the first three groups also, we get—

In Group	Lowest.	Highest.
III.	3	5
" II.	2	6
" I.	1	7

This last part of the law is not at present universally accepted. It implies that the alkali metals, alkaline earth metals, and the elements of the aluminium group can all act with varying degrees of valence, in the same way that the elements of the last few groups can. It is therefore necessary to justify this view.



First, let us consider in what class of compounds would the higher degree of valence be exhibited. A review of the compounds of the elements of the Groups V., VI., VII. shows that they always tend to act with the highest valence when they enter into combination with radicals of a like electrical polarity; but that they tend to act with the lowest degree of valence possible when they enter into combination with radicals or elements which possess an unlike polarity.

For instance, when Cl or I enter into combination with negative radicals, they often act as trivalent elements

(e.g., in ICl_3 and the iodonium compounds, $\text{I} \begin{pmatrix} \text{R} \\ \diagup \diagdown \\ \text{R} \end{pmatrix}$); while

iodine, there is reason to believe, is even acting with a valence of 5 or 7 in some of the "periodates." Precisely the same phenomena takes place in the case of N, S, and other metalloids, as appears from such compounds as N_2O_5 , SO_3 , SCl_4 , P_2O_5 , &c.

But, in sharp contrast, when union takes place with positive radicals, these same metalloids almost invariably act with their very lowest valence.

For example, the halogens almost invariably act towards metals as monads; likewise oxygen as a dyad in the metallic oxides, and N as a triad in the metallic nitrides.

If, therefore, the same rule holds among the members of the first three groups, we should expect them to exhibit their lowest valence when combined with non-metals (*i.e.*, in salts), and their highest when combined with metals. And this is precisely what we actually find occurring. With such precision, indeed, do the alkali metals and the elements of Groups II. and III. act with their lowest degree of valence towards radicals of an opposite polarity, that even to this very day they are commonly regarded as possessing only one degree of valence, because until recently their only well known compounds were of this nature, notwithstanding the existence of such compounds as KI_3 , $RbBr_3$, $CsBr_3$, $CsBr_5$.

But a new class of compounds has of late been brought to light, in which these metals are united with radicals of the same electrical polarity, *viz.*, other metals.

In these compounds, as was to be expected, they show their polyvalent nature with the utmost clearness, as will be seen from the following formulæ (*vide* Neville, "Report on Chemical Compounds contained in Alloys," *Brit. Assoc. Report*, 1900, 131):—

Na.	K.	Ag.	Zn.	Cd.	Al.
$NaHg_2$	KHg_2	Ag_3Sb	Zn_4Ag	$CdAu$	Al_2Cu
$NaCd_2$	KPt	Ag_2Sn	Zn_2Cu	Cd_2Na	$AlCu$
Na_2Pb		Ag_4Sn	Zn_2Sb	$CdAg_2$	$AlAu_2$
Na_3Bi		Ag_2Al		Al_2Au_5	$AlAu_4$
Na_3Sb				$CdAg_4$	$AlAu_4$
Na_3As					Al_2Cu
Na_4Sn					$AlCu_3$
					$AlAg_2$
					$AlSb$

Whatever valency they possess in these compounds, it certainly is not that which they possess in their compounds with non-metals. Indeed, it appears that here they are acting with a variable valence, and in this are behaving in the precisely same way as the non-metals in their compounds with each other.

That these views are also held by the principal workers in this section of metallurgy is made evident from the following quotations from Neville (*loc. cit.*), the significance and importance of which seems to have escaped the notice of chemists:—

"But as the list now stands it offers matter for the consideration of the student of valency. One sees that the compounds of the metals with the metals present—formulæ that we should expect—from the known valency of the elements, but such bodies as $NaHg_2$, $SnCu_3$, $AlAg_2$ are more remarkable. The first of these is evidently a well marked type, which already occurs several times.

"If I rightly understand Prof. Kurnakov ('Sur les combinaisons mutuelles des métaux'), he thinks that Mendeleeff's law of the total valency of an element for O and H being 8 will find application in the formula of alloys, the H being replaced by other metals. In this case the alkali metals which are monovalent to oxygen should be polyvalent in alloys."

It must be emphasised that this law of valency, as embodied in the equation—

$$v^2 - n^2 - 8(v - n) = 0,$$

only holds in the Periodic Table for elements of moderate atomic weight and at normal temperatures. As the atomic weight or the temperature increases, the deviations from the law become more and more marked. These deviations will be made the subject of a later note.

Consider now some properties of the above equation. If v_1 and v_2 represent its roots, we have—

$$v_1 = n \\ v_2 = -n + 8.$$

Hence,—

$$v_1 + v_2 = 8.$$

i.e., the sum of the highest and lowest degrees of valence with which an element acts towards other elements is a constant whose value is 8.

This is a very remarkable relationship. It includes Mendeleeff's observation that the total valency of an element both towards hydrogen and oxygen is 8. And for this reason:—An element tends to act towards radicals of like electrical sign with its highest valence; but towards radicals of an opposite electrical sign with its lowest valence. Now, hydrogen is electro-positive and oxygen is electro-negative. Therefore by observing the valence exhibited by any one element towards each of these two standard elements, we obtain at the same time the measure of its highest and lowest valence. Hence Mendeleeff's law.

Again, re-arranging the fundamental equation we obtain:—

$$n^2 - 8n + 8v - v^2 = 0.$$

The question naturally arises, does this equation place any restriction on the values v can assume? For from the nature of the case, n , the group number must always be real, and v can only have such values as is compatible with this condition. The condition that n should be real is that—

$$8^2 - 4(8v - v^2) = \text{a positive quantity,}$$

i.e., that—

$$(v - 4)^2 = \text{a positive quantity.}$$

So that no matter what value we give to v , positive or negative, n will always be real.

The answer, therefore, is that the equation imposes no restrictions on the values which v can assume.

Some rather remarkable further developments of this valency law are possible, but are deferred for a later occasion.

University of Berlin, May 31, 1902.

THE ELECTROLYTIC METHOD APPLIED TO URANIUM.*

By LILY GAVIT KOLLOCK and EDGAR F. SMITH.

THE purpose of the present communication is to call attention to the conditions under which uranium can be quantitatively determined in the electrolytic way in solutions of the acetate, the sulphate, and the nitrate (see Tables I., II., and III.), and also to record several separations of uranium by the same means from other metals. It is not necessary to comment further upon the form in which the uranium is precipitated or upon the way in which the deposit is subsequently treated in order to weigh it, as those points have received sufficient attention elsewhere (*Am. Chem. Journ.*, i., 329; *Journ. Am. Chem. Soc.*, xx., 279; and Smith's "Electro-chemical Analysis," p. 94).

It was hoped that possibly iron might be separated from uranium in the acetate solution. Direct experiment demonstrated the opposite. The basic iron salt invariably separated when the temperature of the solution rose to 50° C. Further, the presence of iron in the solution apparently retarded the precipitation of the uranium, as none of the hydroxide of the latter separated with a current of 0.18 ampère and 8 volts. On adding chrome-alum to the uranium acetate solution containing 2 c.c. of free acetic acid and increasing the voltage to 20, there occurred

* Contribution from the John Harrison Laboratory of Chemistry. From the *Journal of the American Chemical Society*, xxiii, No. 8.

TABLE I.—*Electrolysis of Uranium Acetate.*

	U ₃ O ₈ present.	29 per cent acetic acid.	Dilution.	Current.	Voltage.	Tempera- ture.	Time.	U ₃ O ₈ found.	Error.
	Grm.	C.c.	C.c.			°C.		Grm.	
1.	0.0986	0.2	125	N.D. ₁₀₇ =0.29 A	16.25	70	5	0.0988	+0.0002
2.	0.0986	0.2	125	N.D. ₁₀₇ =0.3 A	12.2	70	5	0.0989	+0.0003
3.	0.1972	0.2	125	N.D. ₁₀₇ =0.55 A	13.5	70	4	0.1968	-0.0004
4.	0.1972	0.2	125	N.D. ₁₀₇ =0.3 A	10.75	70	6	0.1970	-0.0002
5.	0.1972	0.2	125	N.D. ₁₀₇ =0.135 A	5.5	70	5	0.1966	-0.0006
6.	0.2952	0.2	125	N.D. ₁₀₇ =0.16 A	4.5	75	5	0.2946	-0.0006
7.	0.2952	0.1	125	N.D. ₁₀₇ =0.1 A	4.5	70	7	0.2948	-0.0004
8.	0.2298	0.1	125	N.D. ₁₀₇ =0.09 A	4.25	70	6	0.2297	-0.0001
9.	0.2298	0.2	125	N.D. ₁₀₇ =0.07 A	4.25	70	5½	0.2299	+0.0001
10.	0.2298	0.1	125	N.D. ₁₀₇ =0.05 A	4.0	65	5	0.2299	+0.0001

TABLE II.—*The Electrolysis of Uranyl Nitrate Solutions.*

U ₃ O ₈ present.	Dilution.	Temperature.	Current.	Voltage.	Time.	U ₃ O ₈ found.
Grm.	C.c.	°C.			Hours.	Grm.
0.1222	125	75	N.D. ₁₀₇ =0.035 A	4.6	5½	0.1225
0.1222	125	65	N.D. ₁₀₇ =0.04 A	2.25	7½	0.1218

TABLE III.—*Electrolysis of Uranyl Sulphate.*

U ₃ O ₈ present.	Dilution.	Temperature.	Current.	Voltage.	Time.	U ₃ O ₈ found.	Error.
Grm.	C.c.	°C.			Hours.	Grm.	Grm.
0.1320	125	75	N.D. ₁₀₇ =0.02 A	2	6½	0.1320	—
0.1320	125	75	N.D. ₁₀₇ =0.02 A	2	5½	0.1322	+0.0002
0.1393	125	75	N.D. ₁₀₇ =0.04 A	2.25	5	0.1395	+0.0002
0.1393	125	70	N.D. ₁₀₇ =0.038 A	2.25	7	0.1392	-0.0001

TABLE IV.—*Separation of Uranium from Barium, Calcium, Magnesium, and Zinc.*

	U ₃ O ₈ present. Grm.	Barium present. Grm.	29 per cent free acetic acid. C.c.	Dilu- tion. C.c.	Temper- ature. °C.	Current.	Voltage.	Time. Hours.	U ₃ O ₈ found. Grm.	Error. Grm.
A.—From Barium (Acetates).										
1.	0.1116	0.11	0.5	125	70	N.D. ₁₀₇ =0.02 A	2	5½	0.1119	+0.0003
2.	0.1116	0.11	0.5	125	65	N.D. ₁₀₇ =0.04 A	8	5½	0.1117	+0.0001
3.	0.1116	0.11	0.2	125	70	N.D. ₁₀₇ =0.1 A	4.5	4	0.1117	+0.0001
B.—From Calcium (Acetates).										
1.	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ =0.025 A	2.25	6½	0.1113	-0.0003
2.	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ =0.04 A	2.5	5½	0.1114	-0.0003
3.	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ =0.05 A	2.25	4½	0.1113	-0.0003
4.	0.1116	0.1	0.2	125	70	N.D. ₁₀₇ =0.025 A	2.0	4½	0.1115	-0.0001
C.—From Magnesium (Acetates).										
1.	0.1116	0.1	0.1	125	70	N.D. ₁₀₇ =0.026 A	2.25	6	0.1115	-0.0001
2.	0.1102	0.1	0.1	125	70	N.D. ₁₀₇ =0.05 A	2.25	5½	0.1104	+0.0002
3.	0.1120	0.1	0.1	125	75	N.D. ₁₀₇ =0.15 A	4.0	4	0.1119	-0.0001
D.—From Zinc (Acetates).										
1.	0.1120	0.1	0.1	125	70	N.D. ₁₀₇ =0.021 A	2.25	6	0.1120	—
2.	0.1102	0.2	0.2	125	70	N.D. ₁₀₇ =0.017 A	2.25	6	0.1099	-0.0003
3.	0.1102	0.1	0.1	125	70	N.D. ₁₀₇ =0.02 A	2.2	6	0.1100	-0.0002
4.	0.1102	0.1	0.2	125	75	N.D. ₁₀₇ =0.025 A	4.4	4½	0.1103	+0.0001
5.	0.1102	0.15	0.2	125	75	N.D. ₁₀₇ =0.01 A	2.2	6	0.1105	+0.0003
6.	0.1102	0.2	0.2	125	75	N.D. ₁₀₇ =0.02 A	2.25	6	0.1099	-0.0003

no deposition of uranic hydroxide; the chromic oxide, on the other hand, was converted into chromic acid.

Quantitative results were also obtained by the electrolysis of the sulphate. The neutral salt solution was diluted to 125 c.c. and heated to 75° C., when a current of from 0.02 to 0.04 ampère for 107 sq. cm. of cathode surface and 2.25 volts was passed.

The Separation of Uranium from Barium, Calcium, Magnesium, and Zinc.

In the paper by Smith (*loc. cit.*), to which reference has already been made, he calls attention to the separation of uranium in the electrolytic way from the alkali metals and

from barium. Actual results are given. It seemed desirable to amplify the suggestion; hence the presentation of the results given in Table IV. It may be said here that, in attempting to separate nickel and cobalt, no satisfaction could be obtained, so that eventually that particular line of experiment was abandoned. During the precipitation of the urano-uranic hydrate the dish should be well covered, so that as little evaporation as possible occurs. It was observed that in case of evaporation there was danger of other salts separating upon the exposed metal and on re-filling with water the uranium precipitate was apt to enclose the same and thus carry with it a slight impurity. This precaution is especially necessary in the separation from zinc.

VIDAL BLACK AND ANILINE BLACK.

By M. VIDAL.

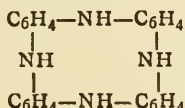
In a previous paper (*Moniteur Scientifique*, September, 1897, p. 655) I described the various phases of the direct formation of my sulphurised colouring materials, and clearly proved the diphenylamine or thiodiphenylamine origin of Vidal black.

I also examined a series of parallel reactions in the formation of aniline black, and I was even able to establish the fact that this latter had, like my black, *p*-amidophenol as a basis.

In fact, if in concentrated sulphuric solution I act on aniline, either by an oxidising agent of a chemical nature, such as bichromate of potassium or by an electro-positive current, I observe in the first place the formation of *p*-amidophenol, which by a graduated hydration of the sulphuric acid, is transformed successively into *p*-amido-oxydiphenylamine and into aniline black; this reaction is also produced with the para-sulphonised derivative of aniline, para-sulphanilic acid, but, with the evolution of sulphurous acid.

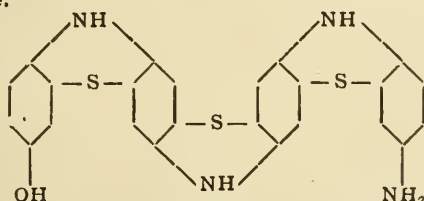
Thus the result of this observation is :—(1) That aniline black has *p*-amidophenol as a basis, this latter being formed in all probability by the transposition of the phenylhydroxylamine obtained in the first place by the oxidation of the aniline in concentrated sulphuric acid ; (2) that aniline black, like Vidal black, is the result of the condensation of the diphenylamine radicals.

This almost confirms the structural formula proposed by Goppelsroeder for aniline black :—

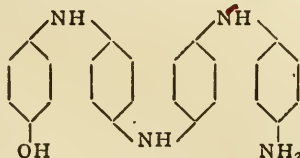


But this formula leaves something wanting; aniline black has the property of becoming green under the influence of certain acid reducing agents, and the green tint thus produced becomes blue in alkaline solution. This fact proves that aniline black should contain one or more active functions, and that the cyclic formula attributed to it by Goppelsroeder will not suffice.

It is necessary to construct a formula with free salifiable groups to explain the property this colouring matter has of being reduced successively under the influence of both reducing and oxidising agents, such as the one I attributed to the sulphurised material para-amido-para-oxydiphenylamine.



Vidal black, from *p*-amido-*p*-oxydiphenylamine.



Aniline black.

Further, the Vidal blacks confirm this hypothesis. While Vidal black from *p*-amido-*p*-oxydiphenylamine has only a slight affinity for alkalis, the Vidal black from *p*-dioxy-diphenylamine, because of its two phenolic functions, combines with soda, giving off a considerable

quantity of heat. But, alike in the case of aniline black as in that of the various sulphur blacks, under the influence of oxidising and reducing agents, and of acids and alkalis, the tints of the colouring materials are either green, blue, or black.

From what has preceded, the analogy of origin, formation, and character appears to be well established between Vidal black and aniline black, and M. Goppelsroeder's formula, with the above mentioned modification, can be applied to aniline black.

Further, the facts I described in my French patent, No. 307,631, January 30, 1901, that is to say, the condensation of *p*-amido-*p*-oxydiphenylamine in the presence of oxidising agents to furnish aniline black has just found an application. According to their patent, No. 313,035, July 27, 1901, the "Compagnie Parisienne des couleurs d'anilins" substitutes *p*-amido-*p*-oxydiphenylamine for aniline to obtain blacks by oxidation.

On the other hand, the piazothiolic formula attributed by M. Geigy to Vidal black and other sulphurised colouring materials is not in accordance with the preceding observations and the methods of production of the different sulphurised materials of the Vidal black series.

The following questions may be asked :—1. How can we explain the formation of the sulphurised derivatives of the thiodiphenylamines with a piazothiolic formula? 2. How can *p*-amidophenol and phenylenediamine give rise to a piazothiolic group, by means of the *p*-dioxy, *p*-diamido, and *p*-amidoxydiphenylamines which they form, when the amido group in the ortho-position with regard to the diphenylamine bond is completely at fault?

Consequently, if the result with aqueous SO₂ at 180° is the same with the diphenylamines having an amido group in the ortho-position, and bodies not able to form diphenylamines possess this essential condition for the piazothiolic formation, it is necessary to reject Geigy's hypothesis for the direct formation of sulphurised colouring materials, especially as the analogies observed between aniline black and Vidal black suffice on their part to destroy it.—*Moniteur Scientifique*, 1902, Series 4, vol., xvi., p. 218.

THE SEPARATION OF GLUCINA.

By G. WYROUBOFF.

THE difficulties met with when we wish to separate glucina from the iron and alumina which always accompany it in emerald, the principal gluciniferous mineral, are well known, especially if we have only to deal with a small quantity of the material.

Carbonate of ammonia dissolves glucina very slowly, and finally dissolves a little alumina if it is not condensed by heat or by prolonged contact with water.

Quite recently (*Bull. Soc. Min.*, 1902, vol. xxv.), while discussing a paper by MM. Rosenheim and Woge on the valency of glucinum, I was led to examine a certain number of its compounds.

Among these compounds one was found which has, however, been known for a very long time, since it was described by M. Debray in his thesis, which is very slightly soluble and which enables us to precipitate almost the whole of the glucina at once. This compound is the oxalate, Gl₂O₃.6(C₂O₃)₃K₂O. At 15° 100 parts of water dissolve 1.4 parts of this salt, and the solubility increases only slowly with the temperature. This salt only contains 9.5 per cent of Gl₂O₃; it therefore follows that the solubility of the precipitated glucina is about 1 part per thousand.

Now, we know that the oxalates of the same formula containing Al₂O₃, Fe₂O₃, and Cr₂O₃ dissolve at the ordinary temperature in two or three times their weight of water.

In this fact there is, as can be well seen, a method of separation, if not quantitative, at least approximate, and, in any case, very rapid. I have endeavoured to apply

this method to emerald from Limoges, which contains, according to an analysis made by M. Lebeau, about 14 per cent of glucina, and I was able to extract a little more than 9 per cent perfectly free from alumina and iron.

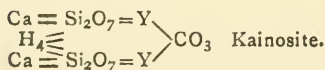
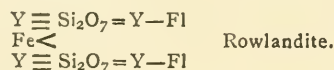
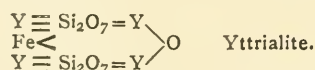
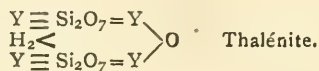
It sufficed to attack the mineral with potash, eliminate the silica in the usual method, evaporate the solution of chlorides to a small volume, and add a concentrated solution of binoxalate of potash. After some time a crystalline precipitate is deposited, which is collected on a filter, and washed with water. The salt, which is very slightly soluble in water, dissolves with ease in dilute acids; it is for this reason that the loss is high, as in the double decomposition, hydrochloric acid is necessarily set at liberty, and remains in the solution.

Perhaps it would be better to neutralise exactly by means of an alkali or to add acetate of soda so as to get better returns, but I have not followed this matter up as it does not really come within the scope of my work, and I only now mention this process of separation because it appears worthy of the attention of those who take an interest in the still so little known compounds of glucina. —*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 14.

THE COMPOSITION OF YTTRIALITE, WITH A CRITICISM OF THE FORMULA ASSIGNED TO THALENITE.*

By W. F. HILLEBRAND.

In a paper describing the new yttrium silicate thalénite (*Bull. Geol. Inst. Upsala*, 1898, iv., 1), the author, C. Benedicks, casts doubt on the formula assigned by Hidden and Mackintosh (*Am. Journ. Sci.*, 1889, xxxviii., 477) to their mineral yttrialite from Llano Co., Texas, for which they deduced the formula $R_2O_3 \cdot 2SiO_2$ or $R_2Si_2O_7$, in which R_2O_3 includes the sesquioxide equivalents of very considerable percentages of monoxides and dioxides. Benedicks would assign yttrialite to a group of which rowlandite is the prototype and to which he believes thalénite and kainosite belong, being either plain basic salts of $H_6Si_2O_7$ of the type $R''R'''_4Si_4O_{15}$ or derivatives in which the fifteenth oxygen atom is replaced by its equivalent in fluorine (rowlandite) or CO_3 (kainosite) as shown below.



Benedicks says: "Dem Yttrialit, von Hidden und Mackintosh beschrieben, sollte die Formel $R_2O_3 \cdot 2SiO_2$ zukommen, worin hauptsächlich Ytter- und Thorerde ist. Dabei wird aber ca. 4% Eisenoxydul in der Analyse vernachlässigt. Wird dies nebst etwas Kalk und Bleioxyd mitgerechnet, so bekommt man die Formel $Fe''O_2 \cdot R_2O_3 \cdot 4SiO_2$, analog mit der des Thalénits, welche besser die Zusammensetzung des Yttrialits wiedergibt, obgleich die Übereinstimmung gar nicht gut ist."

It is, however, not true that Hidden and Mackintosh neglected to take account of the ferrous iron, &c., of their analysis. It was regarded in the derivation of their

empirical formula $R_2Si_2O_7$. How wholly unwarranted was the substitution by Benedicks of his formula for yttrialite is shown by the molecular ratio for $RO : R_2O_3 : SiO_2$, which he gives as 1 : 2 : 4 instead of 1 : 3.25 : 7.42, as calculated by me from Mackintosh's figures, wherein for a sound reason I have converted his UO_3 into UO_2 , thus throwing it with the ThO_2 , where it naturally belongs. The agreement is indeed "gar nicht gut."

Benedicks has made the grave mistake of counting Mackintosh's monoxide bases a second time, thus making a basic salt $R''R'''_4Si_4O_{15}$ instead of the normal one $R''_4Si_4O_{14}$, to which Mackintosh's results closely conform.

Discussion of Benedicks' Formula for Thalénite.

Moreover, in the light of the data furnished by Benedicks himself it cannot be admitted that the formula $H_2Y_4Si_4O_{15}$ for thalénite is established.

Water was determined by him according to Penfield's method (*Am. Journ. Sci.*, 1894, xlviii., 31), but without any hint as to the particular modification employed. If, as seems probable, the water expelled from the mineral was caused to re-condense in the cooler part of the ignition tube, the latter being then weighed and again after driving the condensed water out, two serious sources of error have to be considered: (1) The CO_2 present in the mineral, which would count in part as water unless a very careful correction was made, as provided for by Penfield. No mention is made by Benedicks of any such correction. (2) Nitrogen and helium are said to comprise 1.4 per cent. of the mineral by weight. If so, these would introduce an error in the above water determination of contrary sign to that due to CO_2 , and if the proportion of helium were large this error might be of very considerable magnitude.

In an appendix to his paper Benedicks gives an analysis of what he considers to be a very pure form of thalénite. He makes no comparison of this with his earlier analysis, nor does he deduce a molecular ratio, which I find to be 1 : 2.6 : 5.15, or 1 : 3.03 : 6.02 if small amounts of lime, magnesia, and soda are neglected, instead of 1 : 2 : 4 as required by his formula. There being no CO_2 in this purer material, the value for water (if determined as above surmised) may be supposed to be affected only by the error due to nitrogen and helium. It will be seen that the neglect to regard lime, magnesia, and soda in his second analysis affects the ratio very seriously. This neglect may be justified in figuring on his first analysis because of an approximate balancing by CO_2 , but it would be by no means so in the other in spite of the very satisfactory ratio obtained and leading to the empirical formula $R''R'''_6Si_6O_{22}$, which is susceptible of a variety of interpretations. It may represent a basic salt of diorthosilicic acid $R''R'''_5(R''O)Si_2O_7$, or of metasilicic acid $R''R'''_2(R''O)_4(SiO_3)_6$, or possibly even of other acids.

Finally, if the values for nitrogen and helium are really anywhere near so great as given, an additional argument against the validity of his formula is furnished. For, in the light of Kohlschütter's recent researches (*Ann. der Chem.*, 1901, cccxvii., 158) and my own less conclusive work of a much earlier date (*Bull. U.S. Geol. Surv.*, 1891, No. 78, pp. 76–78), it is in the highest degree probable that nitrogen and helium are not occluded in uraninite and other minerals, but are in chemical combination. Now, if this is so, in a mineral containing as much as 1.4 per cent. of nitrogen by weight this must, quite irrespective of its form of combination, play so important a rôle in the molecule as to utterly invalidate any formula based on calculations from which it is omitted. If the above percentage is made up in large part of helium, its effect, because of its low atomic weight, must be vastly greater than that of nitrogen.

Until light is thrown on the nature of the combinations these two gases form in minerals, no very positive conclu-

* From the *American Journal of Science*, xiii., No. 74.

sions can be reached as to the formulæ to be assigned to those minerals which contain them in more than traces.

Chemical Investigation of Yttrialite.

At the earnest request of Mr. W. E. Hidden, the discoverer of yttrialite, I undertook to re-analyse the mineral in order if possible to settle definitely the question of its composition. This seemed especially desirable since a large quantity of very fine material was available.

The appearance and behaviour of the mineral agreed in all respects except one with those of the original description (*Am. Journ. Sci.*, 1889, xxxviii., 477). It is there stated that the strongly ignited mineral is insoluble in acid. This is a mistake, for when powdered the solubility in hydrochloric acid is even then perfect, although not rapid.

Careful examination of thin sections under the microscope showed a condition that augured ill for decisive analytical results despite the apparently fine quality of the large specimens. Distinctly foreign mineral fragments were as good as absent except for insignificant coatings of a white alteration product, presumably a carbonate, but considerable shading was apparent in the slides, indicative of alteration or intimate contamination in the mass of the mineral itself. However, after treatment with hot dilute hydrochloric acid (whereby much yttrialite was dissolved) followed by dilute sodium carbonate, the clear glassy residue appeared to be improved in appearance and the specific gravity of two samples, each composed of small grains uniform in size for each sample, had risen from 4.596 and 4.590 to 4.654 at 23½° C. and 4.646 at 26° C. respectively. The two sizes were then mixed, giving one sample of about 4.65 sp. gr. at 25° C. That of the unpurified material analysed by Mackintosh was 4.575.

Qualitative tests showed the absence of zirconium, glucinum, and aluminium and the presence of a little more than a trace of fluorine, of a very little carbon dioxide, besides some other gases which were set free by treatment with acids and by fusion with an alkali carbonate.

Silica was separated by two evaporations with hydrochloric acid; lead was then thrown out by hydrogen sulphide.

The earths when finally collected together free from all iron, manganese, uranium, titanium, phosphorus, calcium, and magnesium, were ignited and weighed. No filtrate from a precipitate of earth-oxalates was ever regarded as free from earths till after evaporating, igniting, and re-testing. This is a needed precaution in all similar analyses.

The combined earths were dissolved in nitric acid and evaporated to dryness. A saturated solution of potassium sulphate was poured upon the dry mass, which wholly dissolved, but almost at once began to deposit double sulphates. Solid potassium sulphate was then added in crystals. After twenty-four hours the precipitate was collected on a filter and washed with the precipitant solution. Twice was this precipitation repeated after first dissolving the double salts in acid, precipitating by potassium hydroxide, washing, re-dissolving in nitric acid, and evaporating. Then only was the extraction of the yttrium-erbium group practically complete. From the combined filtrates the soluble earths were thrown out, re-converted into nitrates, and again treated with potassium sulphate, whereby a little further insoluble matter was obtained. Yttrium-erbium oxides obtained from the oxalates gave a light-coloured mixture of 265.6 mol. wt. (108.8 at. wt.), which furnished a pink nitrate solution showing the erbium absorption bands strongly marked, with very faint indications of the strongest band of the didymium components.

The insoluble sulphates were converted into chlorides and thrice treated with potassium hydroxide and chlorine to precipitate thorium and cerium. From the filtrates the soluble earths were recovered and subjected to a repetition of this treatment. Their oxides after purification were

light dirty brown when heated over the Bunsen flame, but greyish white when blasted. Their mol. wt. was 335.5 (at. wt. 143.7); their nitrate solution was pink and gave the characteristic didymium component absorption bands altogether free from those of the erbium constituents.

Cerium and thorium were separated by a combination of the ammonium oxalate and thiosulphate methods. The weighed thoria was pure white, the ceria of a pale salmon colour.

The condition of the uranium was shown by its precipitability as tetrafluoride on dissolving the mineral in hydrofluoric acid. The reaction afforded a ready means of estimating with exactness the ferrous iron by permanganate after rapidly filtering off the fluorides precipitated in an atmosphere of carbon dioxide. Solution of the mineral in a sealed tube with dilute sulphuric acid allowed of finding the oxygen value of both UO₂ and FeO by permanganate. The result thus found for UO₂ agreed marvellously well with that calculated from the U₃O₈ found gravimetrically in a separate portion.

Analyses of Yttrialite.

	Hillebrand.		Mackintosh.	
		Mol. ratios.		Mol. ratios.
SiO ₂	29.63	0.4938	29.17	0.4861
TiO ₂	0.05		—	
ThO ₂	10.85	0.0470	12.00	0.0483
UO ₂	1.64 (a)		0.79 (d)	
Ce ₂ O ₃	3.07		1.86	
La ₂ O ₃ &c. ..	5.18 (b)		2.94 (e)	
Y ₂ O ₃ &c. ..	43.45 (c)		22.67 (f)	
Do.		0.1930	5.30 (g)	0.1864
Do.			4.50 (h)	
Do.			14.03 (i)	
Al ₂ O ₃	—		0.55	
Fe ₂ O ₃	0.76		—	
FeO	1.96		2.89	
MnO	0.88		0.77	0.0655
PbO	0.80	0.0608	0.85	
CaO	0.67		0.60	
MgO	0.16			
H ₂ O + 105 C. ..	0.32		0.79	
H ₂ O - 105 C. ..	0.04			
CO ₂	0.11			
P ₂ O ₅	0.12			
N, He } Diff. .	0.31			
Fl, Alk }				
	100.00		99.75	

(a) Volumetrically; gravimetrically, 1.62 per cent.

(b) Atomic weight, 143.8; molecular weight, 335.6.

(c) Atomic weight, 108.8; molecular weight, 265.6.

(d) Given as 0.83 UO₃ by Mackintosh.

(e) Atomic weight, 162; molecular weight, 372.

(f) Atomic weight, 110.3; molecular weight, 268.6.

(g) Atomic weight, 110.53; molecular weight, 269.06.

(h) Atomic weight, 114.9; molecular weight, 277.8.

(i) Atomic weight, 120; molecular weight, 288.

Nitrogen (?) and helium (?) were obtained quantitatively by fusing the mineral with sodium-potassium carbonate in a current of carbon dioxide, and collecting the gases in a nitrometer over potassium hydroxide. The volume was between 1 and 2 c.c. per grm. of yttrialite. The gases were not further examined.

The analysis is given above, together with that of Mackintosh for comparison.

The ratios of Mackintosh's analysis as calculated above by me are certainly wrong in so far as they are affected by the value for iron, which he assumed to be wholly ferrous. If corrected in accordance with the statement of my analysis, or, what amounts to the same thing for the purpose of illustration and is simpler, if my ratio is altered to conform to his statement for RO and R₂O₃ bases, it becomes 0.0644 : 0.1882, a very close agreement.

It is altogether probable that Mackintosh's separations of the earths were not so far-reaching as mine, and this belief is borne out by the differences in the experimental molecular weights for the lanthanum and yttrium groups, mine being more in accordance with what might be expected, and, moreover, agreeing almost exactly with those which were found by me for rowlandite in 1893, namely, 336.8 and 266.2 respectively.

(The three minerals gadolinite, yttrialite, and rowlandite occur in Llano County in most intimate association, suggestive of close community of origin, a suggestion which is emphasised by the marvellous agreement for gadolinite and yttrialite, not only in the relative proportions of the trivalent earth metals but in their absolute amounts as well.

		Ce_2O_3	La_2O_3	$\&c.$	Y_2O_3	$\&c.$
Gadolinite (Genth)		2.65	5.22		44.35	
" "		2.66	5.01		44.45	
" (Eakins)		2.62	5.22		41.55	
Yttrialite (Hillebrand)		3.07	5.18		43.45	
Rowlandite		5.06	9.34		47.70	

This concordant testimony of three analysts may be regarded as strong evidence of the correctness of the earth separations made by them in these cases. Nearly the same relation is shown by the trivalent earth-metals of rowlandite, as seen in the table above).

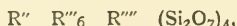
It is, of course, impossible to say what disposition should be made of the small amounts of firmly held water, phosphorus, carbon dioxide, fluorine, and alkalis. The ratios of my analysis are therefore to a slight extent incorrect, but probably not enough to influence any conclusions that may be drawn. One thing is apparent, that the preliminary purification by acid has had no pronounced effect on the composition of the mass acted on, otherwise Mackintosh's and my analyses should show far greater differences in the main constituents.

The crude empirical formulæ deducible from the ratios of the two analyses are nearly—

Hillebrand		R''_{61}	R'''_{386}	R''''_{47}	$(\text{Si}_2\text{O}_7)_{247}$
Mackintosh		R''_{65}	R'''_{373}	R''''_{48}	$(\text{Si}_2\text{O}_7)_{243}$

there being a slight deficiency of oxygen atoms in each case for the radical Si_2O_7 , which is increased by allowing for the CO_2 and P_2O_5 .

In so far then as the character of the acid radical is concerned, the results of Mackintosh's analysis are fully confirmed, and there is absolutely no ground for accepting Benedicks' basic formula, which, as I have already shown, is based on a palpable error. But the ratios are not at all such as to lend themselves to ready resolution into isomorphous salts of the acid $\text{H}_6\text{Si}_2\text{O}_7$. By doing quite unwarranted violence to the analytical data the above formulæ might be reduced to—

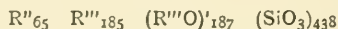


which can be readily represented structurally as a single complex molecule or as a mixture of molecules like $3R''_2\text{Si}_2\text{O}_7 + R''R''''\text{Si}_2\text{O}_7$. In neither case, however, is the type of the rowlandite molecule approached, which requires an altogether different ratio of monoxide, dioxide, and trioxide bases, nor, if the second be accepted, is it at all clear that the two molecules would be mineralogically equivalent, that is, isomorphous.

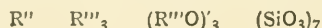
An alternative hypothesis is to regard the mineral as a mixture containing the anhydrous thorite molecule. Proceeding on this assumption and deducting all thorium and uranium and the proper amounts of silicon and oxygen, the crude empirical formulæ become—

Mackintosh		R''_{65}	R'''_{373}	$\text{Si}_{438}\text{O}_{1501}$
Hillebrand		R''_{61}	R'''_{386}	$\text{Si}_{447}\text{O}_{1533}$

which may be interpreted as basic salts of metasilicic acid:—



or—



this last being easily susceptible of symmetrical representation in graphic form.

On the whole I prefer to leave the constitution of yttrialite unsettled until further evidence can be gathered, either from analyses of allied minerals or from yttrialite itself of more certain purity than any that has yet been discovered.

It must not be forgotten that the gases other than CO_2 contained in the mineral may be the cause of the inability to arrive at satisfactory conclusions in the case of this and all other minerals which contain them, as I have already pointed out.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

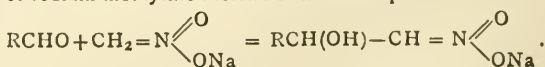
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxv., No. 1, July 7, 1902.

Electrolysis of Silver Nitrate.—A. Leduc.—A bath of silver nitrate, primarily neutral for example, may generally be said to become more and more acid as electrolysis is pursued, if the anode is soluble. MM. Rodger and Watson find, on the contrary, that the acidity of the bath seems to diminish with use. This contradiction is only apparent, the results depending on certain conditions. The author examines solutions with (1) a platinum anode, and (2) a soluble anode. His experiments show that the contra-electromotive force in a voltameter containing nitrate of silver, a substance which is generally supposed to have a very slight or even no electromotive force, is not in reality negligible. His experiments show that this E.M.F. is about 0.3 volt.

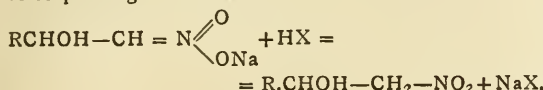
Hydration of Zinc Oxide.—M. de Forcrand.—Anhydrous zinc oxide prepared at 125° is apparently in the least condensed form, and is transformed into normal crystalline hydrate, $\text{Zn}(\text{OH})_2$, evolving $+2.19$ cals. when uniting with water in the liquid state. This is the only result which the author considers to have a precise signification, and it differs from Thomsen's and Massol's results. The condensed anhydrous oxide, prepared at a bright red heat, gives a certain number of different condensation hydrates. The mean value corresponding to the fixation of 1 mol. of water lies between 4.5 and 5 cals. The most hydrated amongst these latter hydrates lose water progressively when they are heated, etherifying themselves and giving meta-zincic acids more and more stable and more and more polymerised. The condensation of $n\text{Zn}(\text{OH})_2$ and its transformation into $(\text{ZnO}, \text{H}_2\text{O})_n$ evolves about $n \times 3.80$ cals. Lime and probably many other metallic oxides give rise to analogous phenomena.

Oxidising Properties of a Pyranol.—R. Fosse.—The author endeavours to prepare hypoiodite of dinaphthopyranoxonium. By analogy with one of the known preparations for the hypochlorite and bromite, he allows hydriodic acid to act on dinaphthopyranol, and was surprised to obtain not the expected hypoiodate but oxonium triiodide. A study of this reaction leads to the conclusion that dinaphthopyranol behaves as an oxidising agent towards HI, and a still more curious example of its oxidising properties is its action on diphenopyranol.

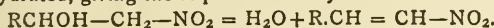
Condensation of Nitromethane with the Aromatic Aldehydes.—L. Bouveault and A. Wahl.—The authors repeat Thiele's experiments on the preparation of nitrostyrolene by performing the condensation by means of sodium methylate instead of alcoholic potash.



These salts are very soluble in water, which does not dissociate them, but acids decompose them, setting free the corresponding nitrated alcohol.



At the moment of its formation, and in varying proportion according to particular cases, this nitrated alcohol is dehydrated, giving the required nitrostyrene.



The authors have also applied this method to condensations of nitromethane with anisic, piperonylic, and ortho-nitrobenzoic aldehydes and with furfural.

Action of Diazoic Salts on Desmotroposantonine and Desmotroposantonous Acid.—E. Wedekind and Oscar Schmidt.—Some years ago M. Wedekind showed that santonic acid combines with diazoic salts in alkaline solution, giving rise to substances having a yellowish red colour, whose constitution was not clearly defined, owing to the instability of these substances and the difficulty of purifying them. On account of these difficulties, the authors now propose to examine the action of the diazoic salts on another isomer of santonine—desmotroposantonine, which was discovered by Andreocci. They succeed in causing desmotroposantonine to combine with the diazoic salts, and obtain a well crystalline and very stable body. Santonine, on the contrary, which does not contain a benzenic radicle, does not combine with the diazoic compounds. In the same way, the authors obtain the azoic compounds of *p*-toluidine, orthonitraniline, *p*-nitraniline, *p*-aminobenzoic acid, sulphanilic acid, and toluidine. All these bodies are well crystallised, have a yellow or red colour, and melt above 260°.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 3.

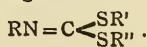
Form in which Silicon occurs in Cast-iron and in Low Percentage Ferrosilicons.—P. Lebeau.—Already noticed.

Action of some Reagents on Amorphous Silicon.—P. Lebeau.—Already inserted in full.

The Cementation of Iron by means of Silicon.—P. Lebeau.—Already inserted in full.

Alloys of Aluminium and Magnesium.—O. Boudouard.—Already noticed.

Imidodithiocarbonic Ethers. Formation, Constitution, and General Reactions.—M. Delepine.—Iodide of methyl reacts on dimethylformocarbithialdine with the production of diethyl formal, of iodhydrate of methylamine, and finally of a crystallised iodhydrate of a sulphurised and nitrated base, $\text{C}_4\text{H}_9\text{NS}_2$, which has been examined from the point of view of its decomposition by hydrochloric acid and ammonia; the formula $\text{CH}_3\text{N}:\text{C}(\text{SCH}_3)_2$ was attributed to the base which made it a dimethyl methylimidodithiocarbonate; that is to say, the most simple trisubstituted term of a new series of compounds having the general formula:—



This constitution was only put forward tentatively, and the author has made a complete research on the question, and now describes numerous and new experiments on these compounds, of which he has prepared ten terms from C_4 to C_{10} .

Imidodithiocarbonic Ethers. Preparation and Properties.—M. Delepine.—To prepare these ethers two molecules of the primary amine are dissolved in two or three times their weight of commercial absolute alcohol in a matras; one molecule of sulphide of carbon is gradually

added; the reaction takes place immediately with the evolution of heat; this is kept down by running water over the matras; as a rule, thiosulphocarbamate crystallises out abundantly on cooling. Two molecules of the halogenised derivative, $(\text{CH}_3\text{I}.\text{C}_2\text{H}_5\text{I})$, are then added, which causes a fresh exothermic reaction; after an hour's time the reaction is over and the liquor barely coloured. On adding 4 or 5 volumes of water nothing is precipitated with the first terms, but, starting from allyl- or propylamine, bad smelling oils are precipitated; these are eliminated by means of ether. The imidodithiocarbonic ethers eventually obtained are mobile, refrangible liquids, perfectly colourless up to C_7 , and slightly yellow above this; they have a powerful odour difficult to define, but something like cooked cabbage for the lower terms. A complete table of the formulæ for the ten terms is given, followed by their analyses and compositions.

The β Diketones.—G. Leser.—The author has examined the most diverse β -ketones, and from the properties of all the products obtained he draws some interesting conclusions from the tautomeric point of view; that is to say, the conditions of molecular equilibrium in which these bodies react, either as true di-ketones or as mono- or di-enolic compounds.

Migration of the Methyl Group in the Molecule of Camphor.—E. Blaise and G. Blanc.—Not suitable for abstraction.

On Monooxybenzalbromindanone.—K. Miniati.—To a warm alcoholic solution of salicylic aldehyde and bromised indanone in molecular proportions, a quantity of caustic soda equal to double the amount of aldehyde used, is added all at once. The liquid takes a red colour for some moments, and then the sodic salt of 2'-oxybenzal-2-bromindanone separates out; this is submitted to repeated crystallisations in alcohol, and brilliant yellow needles are obtained. This body is soluble in warm dilute soda, giving a reddish-yellow colour; on cooling it deposits a pale red crystalline salt. The 2'-methoxy-2-bromindanone is prepared by boiling with acetic anhydride and dried acetate of sodium. The meta-oxybenzal-2-bromindanone is easily formed by following the instructions given for the preparation of the ortho-compound.

Essence of Ylang-Ylang.—G. Darzens.—Wishing to determine the nature of the phenols contained in this essence, and also to discover whether, besides the alcohols already known, other alcohols were present, especially the lower ones of the fatty series, the author took 250 grms. of the pure essence, and instead of saponifying it by means of an alcoholic solution of potash, he effected this by shaking it up in a sealed Wurtz matras with an aqueous solution of potash, the whole being kept hot in a water-bath. After a few moments the solution took a yellow colour, but the mixture was kept at 100° for about ten hours. The aqueous solution was then diluted, and the oily layer washed with water, the washings being added to the aqueous portion. To detect the lower alcohols, the aqueous portion was distilled for a few minutes only, so as to obtain about 10 c.c. only of distillate. This distillate was then saturated with potassic carbonate, when a few drops of a liquid appeared, having the odour and physical appearance of methylic alcohol. These few drops, treated with chloride of benzoyl and carbonate of soda in excess, gave the characteristic odour of benzoate of methyl. The alkaline aqueous solution was then treated with a current of carbonic acid to remove the phenols, and the cloudy liquid formed was exhausted with ether, and the ethereal solution evaporated in a crucible. The residue was taken up in the smallest possible quantity of soda-lye at 10 per cent, and after filtration shaken up with chloride of benzoyl to transform the phenols into benzoylised derivatives. The liquid soon solidifies, when an excess of 10 per cent carbonate of soda is added. The insoluble benzoylised derivative remaining is drained and purified by crystallisation; it was identified as benzoyl-para-cresol. Acetyl-para-cresol was also found.

MISCELLANEOUS.

Appointment.—At a meeting of the Council of the Pharmaceutical Society of Great Britain, held at 17, Bloomsbury Square, on Wednesday August 6th, Dr. William Palmer Wynne, F.R.S., Assistant Professor of Chemistry in the Royal College of Science, South Kensington, was appointed to the Chair of Chemistry in the School of Pharmacy of the Pharmaceutical Society of Great Britain, in succession to Dr. J. Norman Collie, F.R.S., who was recently appointed to the Chair of Organic Chemistry in University College, London.

Institute of Chemistry Examinations.—Pass Lists (July, 1902).—*Intermediate Examination*—24 candidates presented themselves; the following (12) passed: W. L. St. J. Alton, Univ. Coll., London, and under M. W. Blyth, F.I.C.; M. Barrowcliff, Univ. Coll., Nottingham; P. H. Carpenter, Finsbury Tech. Coll.; R. W. Clarke, Finsbury Tech. Coll.; O. C. M. Davis, Univ. Coll., Bristol; J. F. P. Fielding, King's Coll., London; G. W. Glen, Glasgow and W. of Scot. Tech. Coll.; B. F. Howard, Finsbury Tech. Coll.; F. T. Jewson; Univ. Coll., Nottingham; W. H. Keys, University of Birmingham; T. H. Lloyd, Univ. Coll., Cardiff; and E. Smith, Glasgow and W. of Scot. Tech. Coll., and under Dr. A. Thomson, M.A., F.I.C. *Final A.I.C. Examination—Branch "A" (Mineral Chemistry)*—7 candidates presented themselves; the following (3) passed: A. E. Garland, Assoc. Royal Coll. Science, London; J. L. Garle, Univ. Coll., London; G. C. Jones (for Fellowship, F.I.C.), Assoc. City and Guilds Institute, London. *Branch "B" (Metallurgical Chemistry)*—2 candidates presented themselves and passed: W. B. Parker, University of Birmingham; J. C. Sheldon, University of Birmingham, and under A. E. Tucker, F.I.C. *Branch "C" (Physical Chemistry)*—2 candidates presented themselves; 1 passed: H. Bassett, B.Sc. (Lond.), Univ. Coll., London. *Branch "D" (Organic Chemistry)*—6 candidates presented themselves; 1 passed: S. Andrews, B.Sc. (Lond.), Assoc. Royal Coll. Science, London. *Branch "E" (Analysis of Food and Drugs, including Examination in Therapeutics, Pharmacology, and Microscopy)*—8 candidates presented themselves; the following (5) passed: G. J. Alderton, King's Coll., London; R. Clegg, B.Sc. (Aberdeen); E. V. Jones, University of Birmingham; W. H. Roberts, M.Sc. (Vit &), University Coll., Liverpool; H. P. Stevens, B.A. (Oxon.), Ph.D. (Heidelberg), (for Fellowship, F.I.C.). The Examiners in General Theoretical and Practical Chemistry were Dr. Bernard Dyer, F.I.C., and Dr. W. Palmer Wynne, F.R.S., F.I.C. The Examiner in Therapeutics, Pharmacology, and Microscopy was Dr. Arthur P. Luff, F.R.C.P., F.I.C.

The Rhodium Alums and the Separation of Rhodium from Iridium.—A. Piccini and L. Marino.—The authors have succeeded in obtaining rhodium alums, $\text{SO}_4\text{M}_2(\text{SO}_4)_3\text{Rh}_2 + 24\text{H}_2\text{O}$, in regular, yellow octahedra, sometimes having facets of rhombohedral dodecahedra (and even in cubes). They dissolved the hydrate of the sesquioxide of rhodium in dilute sulphuric acid; this gave a bright yellow solution, to which they added an alkaline sulphate, but not in excess or double sulphates would be formed; the solution containing a certain proportion of free sulphuric acid was evaporated in the desiccator, and soon deposited crystals. The caesium salt is one of the most easy to obtain, as it is the least soluble, though much more so than the aluminocæsic alum; it fuses at $110-112^\circ$, giving an orange-coloured liquid; when heated more strongly it loses a portion of its water, and becomes brownish. The rhodium alum closely resembles it, but is more soluble; the potassium salt is still more soluble, and the crystals are very difficult to obtain pure. The ammonium alum, although very soluble, is easily obtained in the form of orange-coloured octahedral crystals, of which the facets attain the size of 1 c.c. square; it is fusible at $102-103^\circ$; on calcination it leaves rhodium

mixed with a little sulphate. Thallium alum is also obtained. Rhodium is the only one of all the metals of the platinum group which forms alums; if the rhodium contains iridium, the crystals of the alum are quite free from this metal. This provides a new method for the separation of rhodium and iridium.—*Zeit. Anorg. Ch.*, vol. xxvii., p. 62.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Chemical Refuse.—I should be glad if any reader could give me a reply as to whether brewery waste waters, &c., could be considered as chemical refuse.—**ENQUIRER.**

TO CORRESPONDENTS.

A. P. I.—We do not think there is such a periodical as you require. It is far better to read a paper which is a little in advance of your requirements than to have one levelled down to your present knowledge.

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1902-3.

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Further particulars on application to the Director—

ALFRED JÖRGENSEN, The Laboratory, Copenhagen, V

THE CHEMICAL NEWS.

Vol. LXXXVI., No. 2229.

ON TERBIUM.

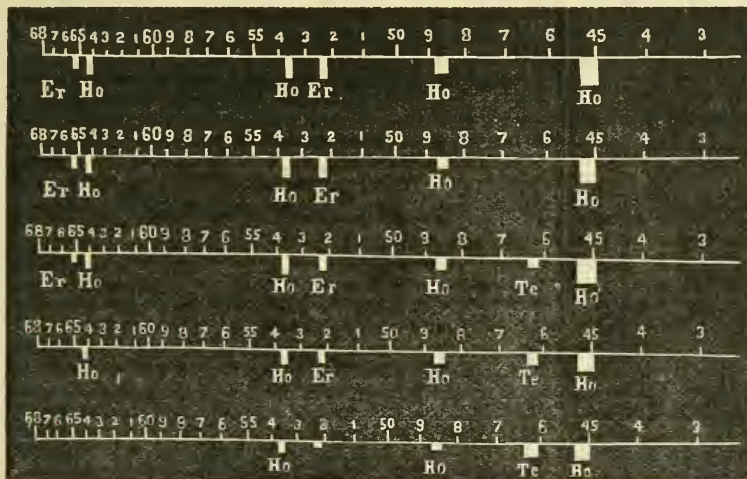
By R. MARC.

Of all the rare earths which have yet been described, the existence of the terbium earth has been most disputed. While French authors, as Marignac (*Ann. Chim. Phys.*, xiv., 247), Lecoq de Boisbaudran (*Comptes Rendus*, cii., 395, 483), Delafontaine (*Ann. d. Chem.*, cxxxiv., 99; cxxxv., 188), and others declare in favour of it, others, such as Bahr and Bunsen (*Ann. d. Chem.*, cxxxvii., 11), Krüss and Hofmann (*Zeit. für Anorgan. Chem.*, iv., 27), call it in question. The atomic weights given to terbium by the several authors vary considerably. Thus, Delafontaine gives 142.5; Marignac, 161; Lecoq de Boisbaudran, 159.48; Crookes, 148.5—149.5.

The following characteristic properties are specified:—A yellow colour, which disappears in a current of hydrogen, colourless salts, no absorption spectrum. Only

1. Terbium oxide possesses a deep brown ochre colour.
2. The earths previously known as terbium earths are mixtures of yttria with another substance, which is much heavier, colourless, and has no spectrum (probably ytterbium); these mixtures are coloured by small quantities of terbium oxide.
3. Terbium forms two oxidation products, of which the higher is coloured and the lower colourless (like praseodymium).
4. Terbium probably possesses an absorption spectrum, which consists essentially of the bands λ 464—461.

My material consisted of the lighter coloured oxides, which were separated by Dr. A. Weiss in the preparation of didymium from monazite by the chromic acid method of Muthmann and Böhm (*Berichte*, 1900, xxxiii., 42—49), and the last fractions were certainly the richest. The oxides had a yellow colour, and showed in the absorption spectrum bands of erbium, neodymium, and samarium. After neodymium and samarium had been removed by treatment with potassium sulphate, according to Bettendorf's method (*Ann. d. Chem.*, cclxx., 376), the residue, which only showed the bands of erbium, was fractionated with ammonia, when the oxides obtained from the alkaline solution became, fraction by fraction, darker, and finally deep brown coloured, while the erbium spectrum disappeared gradually from them, and at the same time a



Fraction 20.—Yellow. At. wt., 143.3.

Fraction 14.—Dark yellow.

Fraction 10.—Brown.

Fraction 6.—Deep brown ochre.

Fraction 1.—Deep brown ochre. At. wt., 164.8.

Delafontaine asserts that the salts are sometimes of a faint amethyst colour, and that the solutions of the salts possess a spectrum, which is composed of the following three bands:—

- λ 522
- λ 497?
- λ 495 (strong)

Krüss and Hofmann proved that the yellow oxide, which Marignac and Lecoq regarded as a compound of terbium, is not a single substance. A yellow earth, prepared according to the directions of these two authors, which had an atomic weight of 158.4 and could not be decomposed by the method of separation used by Marignac and Lecoq, they split up by means of a new method of separation into a series, the first member of which had an atomic weight of 152.4, and the last 163.

We also by a special method of separation have succeeded in decomposing into a series of 4 members an earth, which corresponded to the preparations of terbium of the above authors, and possessed an atomic weight of 158; the atomic weights of the first and last members of the series were respectively 152 and 161. Exhaustive researches have, however, led me to interpret this result differently from Krüss and Hofmann. My results may be shortly stated as follows:—

new band λ 464—461 became visible, and increased in intensity. After a very long series of fractionating I succeeded in almost entirely getting rid of the erbium spectrum, while the band λ 454—449 was still fairly distinct, and the bands λ 640, 536, and 522 were only faintly visible. These four lines, according to Soret, are characteristic of holmium. The band λ 464—461 was clearly visible.

The dark colour of the material was very surprising; as spectroscopic examination showed that it was quite free from didymium, the colour must have been due to another earth. Hitherto terbium has been described only as dark yellow. But as the method of preparation from the erbium-holmium material by means of ammonia would allow of terbium being included, it might be supposed that the latter was present in a higher degree of purity. The atomic weight of this fraction was therefore determined. It amounted to 158 for R_2O_3 .

Thus, this number was similar to that ascribed to terbium by previous authors—Marignac and Lecoq—which seemed singular, considering the great difference in the colour of the materials.

I now endeavoured to determine whether an alteration in the atomic weight would be produced by further fractionating with ammonia. However, this was not the

case. Next I tried to fractionate with oxalic acid. This was done by adding hot concentrated oxalic acid to the concentrated solution of the earths in very strong hydrochloric acid in a little flask, until the solution became slightly cloudy; then the flask was cooled rapidly, so that a very fine crystalline precipitate of oxalate was formed. Thus I succeeded by four such fractionatings in decomposing the earth in such a way that the first member had an atomic weight of 161.18, and the last 151.93. Thus this decomposition corresponds, as has already been pointed out, to that effected by Krüss and Hofmann.

The colour of the oxide in fractions 1 and 4 was approximately unchanged. This circumstance, together with the fact that Marignac's and Lecoq's earths with equal atomic weight were yellow, leads us to infer that the coloured earth cannot have great influence on the atomic weight of the preparation; that is, that it can only be present in small quantity. This supposition was confirmed by the following facts:—

Lecoq (*Comptes Rendus*, cii., 359, 483) had already observed the formation of the superoxide of terbium, and determined the mass of the earth which is converted into superoxide. This quantity, according to his determinations by the method of calcination, amounts to 0.71—0.69 per cent of the total earth.

On dissolving my preparation in hydrochloric acid I observed an evolution of chlorine, and made use of this action to determine by titration the quantity of the earth which is converted into superoxide. By adhering to certain conditions, further specified below, I succeeded thus in obtaining nearly constant results, which were as follows, for the earth with atomic weight 158.

I. 0.9795 grm. oxide; 0.7 c.c. $\frac{1}{10}N$ $Na_2S_2O_3 = 0.00056$ grm. O = 0.058 per cent O.

II. 0.7040 grm. oxide; 0.59 c.c. $\frac{1}{10}N$ $Na_2S_2O_3 = 0.00047$ grm. O = 0.066 per cent O.

Now, if we assume that the formation of superoxide takes place according to the equation $R_2O_3 + O = R_2O_4$ we get, taking for R the value 158 obtained by me, the mass of the earth which is converted into superoxide equal to 1.37 per cent and 1.56 per cent, thus on an average about 1.48 per cent.; that is, about twice the quantity which Lecoq found for his darkest earths.

The considerable difference in the two determinations is to be explained by the peculiar behaviour of the earth on calcination, which I shall discuss below.

In a current of hydrogen, the brown earths lost their colour. Now, if the brown colour was caused by the terbium contained in them, a loss of weight must occur on decolorisation in a current of hydrogen, which would correspond to the amount of superoxide determined by titration. After a suitable method, which will be described hereafter, had been discovered, determinations of the material with atomic weight 151.93 were performed by titration and in a current of hydrogen; these agreed fairly well.

The mean of the determinations by titration was 0.073 per cent O, and by reduction 0.069 per cent O, whence the masses of the earth converted into superoxide for the atomic weight 151.93 come to 1.68 per cent and 1.58 per cent respectively. These results confirmed my supposition that the substance to which the colour is due is contained in the material in question in small quantity only—in my case about $1\frac{1}{2}$ per cent—and exercises no appreciable influence on the atomic weight.

That such a small quantity should have so great an effect on the colour is not unusual. For instance, if 2 per cent iron oxide is added to yttria, the mixture dissolved, precipitated, and ignited, a deep red-brown mixture is obtained. Similarly 1—2 per cent praseodymium oxide colours chalk under the same conditions an intense brown. One-tenth per cent manganese dioxide gives to chalk a distinct brown colour; one-tenth per cent praseodymium behaves similarly; while in 10 per cent solution a stratum 5 c.m. thick of this mixture yields no spectrum. This is

probably the reason why earlier investigators have not observed the terbium band λ 464—461.

The hydrous salts of my terbium preparations were coloured, thus agreeing with Delafontaine's observations, only the colour must rather be described as flesh colour. Probably the colour of the terbium salts is itself very intense, as is the case with praseodymium salts, which, when present to the extent of about 1—2 per cent, colour the salts of colourless earths with almost the same intensity.

We now return to the behaviour of the terbium preparations, and have to describe the methods which were employed for the titration and determination in a current of hydrogen.

When dry or slightly moistened, the preparations on addition of hydrochloric acid give off chlorine. If, on the other hand, they are suspended in much water, no perceptible evolution of chlorine occurs until they are heated to boiling.

I used the following method for titration:—The dry oxide was moistened with a few drops of water, and some cubic centimetres of a mixture of concentrated hydrochloric acid and potassium iodide solution were added, and the whole allowed to stand in darkness for an hour. The iodine set free was then titrated with thiosulphate.

The behaviour of the earth on igniting presented a difficulty, for the weight first increased a little and then decreased, and only became approximately constant on very strongly heating.

For the determination of the terbium superoxide in a current of hydrogen, the ordinary method, *i.e.*, heating the oxide in a little boat, could not be used, as the reduced oxide attracts moisture with great energy and increases in weight while it is being taken out of the tube and weighed. But by more protracted action of the hydrogen in a Rose's crucible complete reduction may be effected. Therefore I made the determinations in a Rose's crucible, which fitted into a weighing tube with an air-tight stopper. The crucible and weighing tube were weighed together. After reduction the whole was allowed to become quite cool in a current of hydrogen, the hydrogen was expelled by a current of carefully dried air, and the crucible immediately shut up in the weighing tube. To avoid errors, the crucible had to be filled with dry air when weighed before reduction. During reduction the crucible must be strongly heated with a Bunsen burner. On heating moderately decolorisation results with an increase of weight, which peculiarity is to be explained by the fact that the water formed on reduction at once enters into combination, forming a hydrate.

The increase begins simultaneously with change of colour at 250° and increases up to 350°. At this temperature no further increase takes place. At a red heat the decrease begins; at a bright red heat the weight becomes constant. The maximum increase amounts to 0.0089 per cent, the maximum decrease to 0.07 per cent.

For oxidation it is sufficient to ignite in air, but to obtain constant values the ignition had to be performed with a good blowpipe burner. On igniting in a current of oxygen no further increase of weight took place. The determinations had to be made with a fairly considerable quantity of material (not less than 3 grms.), as otherwise it was impossible to detect the increases by weighing.

There has always been much discussion about the position of the rare earths in the Periodic System. This question has been solved with any degree of certainty only in the cases of a few, *e.g.*, scandium, yttrium, lanthanum.

During my work I have noticed that it seems possible that the other earths may be collected, according to atomic weight, into certain groups, as is the case in the ninth group of the Periodic System. The accompanying plan will illustrate this. (See next column).

The behaviour of the oxides on fractionating also confirms the grouping.

If a raw material is decomposed by means of potassium sulphate into two parts, about half the double

I. More Feebly Basic than Yttria.

Ytterbium	Holmium	Erbium	Terbium
173	164 (166—160)		?

II. More Strongly Basic than Yttria.

Gadolinium	Samarium	Neodymium	Praseodymium
156	150	143	140

If we compare the properties of any two elements in a vertical column, we arrive at the following results:—

Ytterbium ..	Oxide colourless	No spectrum
Gadolinium ..	Colourless salts	
Holmium ..	Oxide yellow	Absorption spectrum
Samarium ..	Light yellow salts	
Erbium ..	Oxides rose coloured and dove grey	Absorption spectrum
Neodymium ..	Red salts	
Terbium ..	Oxides deep brown	Absorption spectrum
Praseodymium	Coloured salts	

Form two oxidation products.

salt is precipitated, and the rest remains in solution, so that Series I. is found chiefly in the solution and Series II. chiefly in the crystals. In the case of Series II., the solubilities of the double salts in a saturated solution of potassium sulphate have been determined by Delafontaine (*Comptes Rendus*, xc., 221), and amount to about—

1 : 150—200 for Gadolinium (Ya) potassium sulphate.			
1 : 2000 "	Samarium	"	"
Almost insoluble, Didymium	"	"	"

(Note.—Bettendorf (*Ann. d. Chem.*, cclxx., 376) also determined the solubility of pure gadolinium in a saturated solution of potassium sulphate by introducing the earths in the form of a concentrated neutral solution of nitrate into saturated potassium sulphate, and allowing to stand for three days. He found 0.76 grm. oxide to 100 parts by volume of solution. I also prepared pure gadolinium (atomic weight, 156.33), and employed the potassium sulphate method, but I did not let the potassium solution stand, but shook it in a shaker for three days. By this method the solubility was found to be decidedly smaller. In 500 c.c. potassium sulphate solution it amounted to 0.44, 0.45, 0.47, 0.47, 0.46. Thus the mean was 0.46, which represents a solubility of less than 1 : 1000. Thus it is clear that the solutions become strongly supersaturated on standing without agitation).

The order of the members of the series becomes apparent on examining the rapidity with which the double salts are precipitated from a saturated solution of potassium sulphate. Praseodymium is precipitated at once; then neodymium; samarium, after from ten to twenty-four hours; and, finally, after shaking for some days, gadolinium.

The potassium double sulphates of Series I., on the other hand, are very easily soluble in potassium sulphate. Their behaviour towards ammonia determines their order. The order of their basicity, as far as can be deduced from the changes of atomic weight and the spectra in the several fractions, is ytterbium, erbium, holmium, terbium.

Arguing from analogy, I should infer from the above table that the atomic weight of terbium is 157.

An article by Biltz has recently appeared (*Berichte*, 1902, xxxv., 562), in which he proposes to arrange the elements of the ninth group in the eighth group, always denoting the three connected elements by the symbol of the best known of them with a preceding X. Thus, XFe would be the symbol for the elements (Mn, Fe) Co, Ni; XPd for Ru, Rh, Pd. In the same way, he recommends collecting the elements of the rare earths as follows:—(La, Ce) Pr, Nd, denoting them by XCe. He expects that in time it will be found possible in this way to arrange in order in the Periodic System the remaining elements of the rare earths. The grouping mentioned by me above

seems to admit of the possibility of such an arrangement. Then the two following groups—

(La, Ce)	Pr, Nd, Sa, Gd
	Te, Er, Ho, Yb

with atomic weights—

(138, 140)	140, 143, 150, 156
(157?)	164 173
	(160—166)

would be denoted by XCe and XEr, and put in the place of lanthanum and ytterbium. Whether cerium, as Biltz assumes, really belongs, not to Group IV. between zirconium and thorium, but to Group III., may be left undecided.

If now we examine from the above point of view the earth containing terbium which we have described, there can be no doubt that it consists of a mixture of ytterbium earth and yttria, coloured by 1½ per cent of terbium oxide. Unfortunately, there was not sufficient material to isolate the ytterbium earth. On the other hand, I was able by a series of 20 fractions so to split up the earth containing terbium (12 grms. in all) that the first member had an atomic weight of 164.8, and the last 143.3. The spectra of fractions 1, 6, 10, 14, 20 were examined, and are reproduced in the diagram given on page 73.

Fraction 1 had the weakest holmium spectrum, while the lines λ 464—461 were very strongly developed. This fraction was also the darkest coloured. Fraction 19 was comparatively light in colour and showed the holmium spectrum fairly distinctly; next to it two erbium bands, but scarcely any indication of the band λ 464—461. The spectra of the other fractions were intermediate between these two.

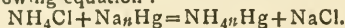
Cleve (*Comptes Rendus*, xci., 328, 381) in his article on erbium earths described a third component of erbium, which he named thulium, and which is said to have an atomic weight of 171. From a great number of different erbium materials I have prepared tables of comparison for spectrum analysis and have examined a long series of fractions, but have not been able to discover anything which would lead us to infer the presence of a third component in erbium. Hence, I think that Cleve's thulium was a mixture of ytterbium and yttrium adulterated by varying quantities of holmium and terbium, just as the decipium oxide belonging to the second series of the above system is probably to be regarded as a mixture of gadolinium oxide and yttria, coloured by praseodymium. Lecoq de Boisbaudran (*Comptes Rendus*, lxxxix., 516) has already proved that philippium, and Soret's X are identical with holmium, and mosandrium with terbium. As regards Demarcay's (*Comptes Rendus*, cxxii., 1484) recent announcement of the discovery of europium, which is characterised by its spectrum of cathode luminescence, that may be explained by the experiments on the spectra of cathode luminescence lately published by us (*Berichte*, 1901, xxxiv., 2460).—*Berichte*, 1902, xxxv., 389.

Sub-oxide of Lead.—S. Tanatar.—The author has taken up the examination of the sub-oxide of lead obtained by Boussingault by the calcination of oxalate of lead. The product formed always contains more lead than it should according to the formula Pb_2O ; this is no doubt due to the reducing action of the atmosphere of carbonic oxide. But if the operation is carried out in a current of carbonic acid, at a well regulated temperature as low as possible, a fine greyish-black powder is obtained, unaltered in dry air, insoluble in, and unchanged by, water, but decomposed by heat, or by alkalis and acids, into metallic lead and PbO . On analysis the material gives 47.72—48.90 per cent of lead (calculated for Pb_2O , 48.14 per cent). The calorimetric examination of the attack with acetic acid, and that of its density, viz., 8.342, shows that we have really to deal with a true sub-oxide of lead, Pb_2O , and not with a mixture of Pb and PbO . If during its preparation, the desired temperature is exceeded, a greyish-green powder is obtained which consists of $Pb + PbO$.—*Zeit. Anorg. Ch.*, vol. xxvii., p. 304.

AMMONIUM AMALGAM.

By HENRI MOISSAN.

THE curious experiments of Leeteck and Tromsdorff, of Berzelius and Pontin, as well as those of Sir Humphry Davy, establish the existence of a so-called ammonium amalgam without definitely showing its composition. This amalgam is obtained by gently shaking up pasty sodium amalgam with a saturated solution of hydrochlorate of ammonium. The reaction has been represented by the following equation:—



The accuracy of this formula has not been verified either by the weights of the materials used or by the volumes of the gases given off.

According to the researches of Gay-Lussac and of Thénard, this amalgam prepared in an aqueous solution of hydrochlorate of ammonium contains $2\frac{1}{2}$ volumes of ammonia for each 2 volumes of hydrogen.

By regarding the ammonium as the radical of the ammoniacal salts, and giving it the symbol NH_4 , it ought to contain a volume of ammonia, double that of the hydrogen, according to the equation:— $(\text{NH}_4)_2 = 2\text{NH}_3 + \text{H}_2$.

The figures given by Gay-Lussac and Thénard are decidedly different to these theoretical figures; however, there is nothing surprising in this, considering the difficulties of these experiments.

After having prepared ammonium amalgam by electrolysis, Landolt observed that on decomposition it gave 2.15 to 2.40 volumes of ammonia gas for 1 volume of hydrogen. But he also noticed that this amalgam did not bring about any double decomposition with the salts of copper and silver, that it differed from the amalgams of potassium and sodium, and that while containing the group NH_4 it ought not to be looked upon as a metallic amalgam. As a matter of fact, we are not much further advanced to-day than at the time when Landolt published his paper. We are still asking whether the ammonia and the hydrogen are combined in this amalgam, forming NH_4 , or whether these two gases are present in the form of an emulsion in the mercury.

Numerous researches have been made on this subject, and delicate measurements have been carried out without any definite conclusion being arrived at. Further, ammonium amalgam has only been examined, up to the present, at the moment of its decomposition. At the same time, interesting researches have been carried out on new compounds, the ammonium metals of which we have spoken in previous papers.

Other researches were attempted on the solubility of different bodies in liquid ammonia. In this connection we may refer to the work of Seeley, of Gore, and of Franklin and Krauss.

Finally, in some very curious experiments, C. Frenzel, taking up the question at its true starting-point, tried first of all what the conductivity of the ammoniacal liquid was. He showed by means of his delicate experiments that this conductivity diminished with the purity of the ammonia, and that it was comparable to that of water. But to sum up, in spite of these experiments and other researches, among which we may mention those of Le Blanc, Goodwin, Kay-Thomson, Pocklington, and Cohen, ammonium has not yet been isolated.

This question of the reaction of an alkaline amalgam on an aqueous solution of an ammoniacal salt is more complex than it has yet been considered to be.

M. Berthelot has already called the attention of chemists to the part played by alkaline amalgams, and particularly to the action of the definite amalgam, Hg_{12}Na , of MM. Krant and Pope in solution in mercury.

We know that these amalgams are used in organic chemistry as hydrogenising agents, for fixing hydrogen by inverse substitution on chlorised bodies, for example, or for transforming the aldehydes or the ketones into alcohols (Friedel and Würtz). M. Berthelot has pointed

out that during these hydrogenising reactions, these amalgams always give off more heat than is given off by the corresponding amount of free hydrogen. This thermic excess joined to the particular action of the reactions developed by the alkalis, accounts for what has up till now been called the nascent state. This interpretation was put forward by Berthelot in 1865.

In taking up the examination of the so-called ammonium amalgam, the first question to be solved consists in accurately measuring the volumes of hydrogen and ammonia given off by the amalgam at the moment of its decomposition. But, on the other hand, the solubility of the ammonia in water is so great that none of the experiments attempted in the presence of this liquid were beyond criticism.

The desiccation of a pasty mass already in the act of decomposing, by means of filter-paper, is absolutely illusory. It is therefore necessary to produce this amalgam in another liquid than water.

This result has been obtained by reacting with chloride of ammonium, in solution in liquid ammonia, on sodium amalgam. The experiment is extremely simple, and is made at -35° ; chloride of sodium is obtained, slightly soluble in the excess of ammonia, as well as a stable metallic mass which increases in volume as soon as it reaches the ordinary temperature.

We first made quite sure that the sodium amalgam kept for several hours in the presence of liquid ammonia between -35° and -39° produced no reaction. We then placed the pasty sodium amalgam in the presence of liquid ammonium into which a small quantity of perfectly dry iodide of ammonium had been dropped. Under these conditions the amalgam reacted on the ammoniacal salt and became more fluid, but without giving off any gas. After prolonged shaking, the amalgam was washed several times with liquid ammonia, and decanted to remove the iodides of ammonium and sodium.

The metallic mass is then cooled down to -80° . At this temperature it appears as a very hard but easily manipulated metal. It is then removed from the vessel in which the reaction has been effected, washed several times with dry ether cooled down to -80° , and saturated with hydrogen. This piece of metal is then placed in a small glass tube, and sealed to a mercury pump. A vacuum is produced, still keeping the temperature down to -80° or -90° . Under these conditions an excellent vacuum can be maintained without any decomposition taking place.

The experiments were made possible by the fact that the so-called ammonium amalgam is able to be formed at -38° or -39° in liquid ammonia without undergoing any decomposition. We made certain that no gas was given off at the moment of the reaction.

So that the double decomposition might be produced with facility, the ammonia was allowed to reach its boiling-point, -33.5° , and if the ammonium amalgam is not too concentrated only a small quantity of ammonia is collected, entirely soluble in water.

When the ammonium amalgam is thus enclosed in a glass tube at a temperature of -80° it is allowed to decompose slowly, gradually reaching the ordinary temperature. At about -40° the mass begins to exude a few drops of mercury; it then takes a liquid form, and as the temperature rises a slight swelling begins to take place. At -30° the mass increases in volume in a very distinct manner, and at $+15^\circ$ it almost entirely fills the glass tube, occupying a volume twenty-five to thirty times greater than the original volume of the amalgam.

During this decomposition it is remarked that the temperature of the tube rises to 5° or 6° above the surrounding temperature. This evolution of heat was constant in all our experiments.

The evolution of gas goes on thus in the vacuum which must be constantly maintained for twelve to fifteen hours. It is very easy to make the decomposition more rapid by heating the amalgam by means of a spirit-lamp.

In some experiments we substituted washing with liquid sulphurous acid or ether saturated with hydrochloric acid gas for the washing with ether.

The results obtained were the same as far as concerns the proportion of ammonia and hydrogen, although under these conditions a certain amount of the amalgam was destroyed. If the gas collected is all put together and analysed, we find that it consists of two volumes of ammonia for one of hydrogen. This is plainly shown by the figures given below:—

Experiment.	Total volume.	H.	NH ₃ .
	C.c.	Per cent.	Per cent.
1	294.72	33.3	66.7
2	264.82	33.4	66.6
3	121.00	33.9	66.1
4	102.31	33.3	66.7
5	528.00	33.3	66.7
6	48.73	33.3	66.7
7	74.82	33.7	66.3

The ammonia was collected in water and titrated or weighed in the form of hydrochlorate of ammonia. The hydrogen was estimated by means of the eudiometer.

In this series of analyses the radical NH₄, corresponding to 2 volumes of ammonia, and 1 volume of hydrogen, would thus seem to exist in the metallic mass prepared at -39°; we are inclined to think, however, that such is not the case. In reality, the hydrogen of the hydriodic acid would appear to furnish a simple or double ammoniacal metallic hydride, and it is the decomposition of this hydride that produces the increase in bulk.

This new interpretation which we are still studying can be applied to the following experiment:—If we react with pasty sodium amalgam on ammonia, we get a slow disengagement of hydrogen without any swelling up. On the other hand, if we react on the same liquid with sodic hydride in solution in sodium amalgam, we obtain an increase in bulk with the production of a butyrous mass which remains for two or three days in the ammoniacal solution.

To prepare this sodic hydride, we started from the interesting experiments made by MM. Troost and Hautefeuille, who have observed that on passing a current of pure hydrogen over sodium kept at a temperature of 350°, a hydride, Na₂H, is formed, having a metallic appearance, and comparable to the hydride of palladium. The solubility of the hydrogen in the sodium is reasonable, but in reality the phenomenon is more complex.

If we keep sodium in a glass U-tube at a temperature of 320° by means of a Darcet metallic alloy bath, we notice that eventually, at the same time that the hydrogen is dissolved in the sodium, a transparent crystallised product is formed, which is produced this time by the combination of the sodium and the hydrogen.

This new compound is comparable with hydride of calcium which we have previously described. When finely powdered, it takes fire on contact with the air; it bursts into flame with a very slight elevation of temperature in chlorine or oxygen gas; it is very hygroscopic, and decomposes with violence on contact with water, giving sodium and hydrogen. This new hydride of sodium can be separated from the excess of metallic sodium by means of liquid ammonia free from moisture.

The alkaline metal is carried off in the form of sodammonium, and the white hydride remains as a residue.

To sum up, from these preliminary experiments we are able to conclude that by reacting with chloride or iodide of ammonium, in solution in anhydrous ammonia, on sodium amalgam, we obtain a metallic mass in which the hydrogen and the ammonia are found in stable combination at -39°.

This metallic mass, through its decomposition at the ordinary temperature in the absence of water, increases its volume thirty times, and gives off 2 volumes of ammonia gas for 1 volume of hydrogen gas.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 14.

THE CALCULATION OF ATOMIC WEIGHTS.

By F. W. CLARKE.

IN the ordinary discussion of ratios relative to atomic weights, different results may be obtained by varying the method of computation. This is due to the fact that the ratios as measured are not absolute, but subject to errors, which should be, but are not usually, distributed. In most cases the tendency is to accumulate all errors, accidental or systematic, upon the constant which is last determined, a procedure which is obviously unscientific. Take, for example, the ratio CaF₂:CaSO₄, upon which our knowledge of the atomic weight of fluorine chiefly depends. In the actual measurement certain errors of observation occur; the data are reduced with assumed values for the atomic weights of calcium, sulphur, and oxygen, which are themselves, to a greater or less extent, inexact, and all of these inaccuracies are brought together in the final result of calculation. If oxygen be taken as the standard of atomic weights, and therefore not subject to error, the atomic weight of fluorine will contain the error of the experiment, plus the errors in the atomic weights of calcium and sulphur; and whether these compensate one another or not we have no means of knowing. Moreover, each error exerts its maximum effect, whose extent can hardly be estimated.

It is generally agreed, with but few dissenting voices, that the work of Stas upon some of the more fundamental atomic weights, is as accurate as the present resources of experimental chemistry can make it. And yet, even here, discrepancies exist which the ordinary method of calculation fails to reconcile. The ratios measured by Stas have been discussed by various writers, especially by Stas himself, by Ostwald, by Thomsen, and by Van der Plaats, and the results of the several computations vary with the method of calculation. Van der Plaats (*Comptes Rendus*, cxvi., 1362), in particular, has illustrated this fact by making two calculations, giving the ratios equal weight in one (A), and weight inversely proportional to the squares of their probable errors in the other (B). In the following table the various results of the reductions appear:—

	Stas.	Ostwald.	Thomsen.	Van der Plaats (A).	Van der Plaats (B).
Ag ..	107.930	107.9376	107.9299	107.9202	107.9244
Cl ..	35.457	35.4529	35.4494	35.4516	35.4505
Br ..	79.952	79.9628	79.9510	79.9407	79.9548
I ..	126.850	126.8640	126.8556	126.8445	126.8494
Na ..	23.043	23.0575	23.0543	23.0453	23.0443
K ..	39.137	39.1361	39.1507	39.1414	39.1403
N ..	14.044	14.0410	14.0396	14.0421	14.0519
S ..	32.074	32.0626	32.0606	32.0576	32.0590
Li ..	7.022	7.0303	7.0307	7.0273	7.0235
Pb ..	206.926	206.911	206.9042	206.9089	206.9308

The differences thus shown are slight, but in the case of bromine they amount to more than two in the second decimal place, an uncertainty greater than is commonly recognised. It is an uncertainty which affects all other determinations depending upon the atomic weight of bromine as an antecedent factor, and which ought to be appreciably diminished. With sulphur and nitrogen the divergences are proportionately even greater.

Now, bearing in mind that the so-called determination of atomic weights is nothing more than the accurate measurement of chemical ratios, let us consider how the latter are to be treated. In the case first cited, the ratio between calcium fluoride and calcium sulphate, the usual method of calculation, is evidently defective, and yet, with existing data, it is the only practicable mode of procedure. With adequate data the ratio should contribute to our knowledge of at least three atomic weights, those of fluorine, calcium, and sulphur, its errors of observation being divided into three parts and not concentrated upon a single factor. That is, the ratio should be combined with other ratios in such a manner that several atomic

weights might be simultaneously computed, all errors being so distributed as to reduce their influence to a minimum. With some groups of ratios calculations of this sort are already possible, and Van der Plaats's reduction of Stas's determinations is a good illustration of my meaning. In this case 23 ratios, involving the atomic weights of 10 elements, were combined into one group of normal equations, and the latter were then solved once for all. The method followed was the well-known method of least squares, and that is the only process which satisfies all conditions. Given enough data of sufficient accuracy, and the method of least squares is applicable to the problem in question; with insufficient evidence or doubtful measurements no solution is satisfactory. The mathematical operations are well understood; it is for the chemist to furnish suitable material to which they may be applied.

In order to illustrate more fully the foregoing considerations, I have combined thirty ratios, involving the atomic weights of silver, chlorine, bromine, iodine, nitrogen, sodium, and potassium, into seven normal equations, in which the constants named appear as the unknown quantities. The ratios are given on pages 53 and 70 of my "Re-calculation of the Atomic Weights" (Smithsonian "Constants of Nature," 1897, Part V.), and contain, in addition to the work of Stas, determinations by Berzelius, Penny, Pelouze, Marignac, Dumas, Gerhardt, Maumené, Turner, Millon, Huntington, Richards, Ramsay and Aston, Hardin, Thomsen, and Hibbs. In short, all determinations of the ratios in question, made up to 1897, are included in the discussion, in order that the effect of such a combination may distinctly appear. The basis of calculation, the standards of reference, are $O = 16$ and $H = 1.0079$, these values being taken as known. Personally, I prefer the hydrogen unit as a starting-point, but in the present case the results are to be compared with those of other computers, as previously cited.

To show the method of calculation, let me first take one or two ratios separately. For instance, the ratio $Ag:Br::100:74.080$ may be written $100\ Br = 74.080\ Ag$, when the symbols Br and Ag represent the two atomic weights respectively. So, also, the ratio $KClO_3:O_3::100:39.154$ becomes in linear form $39.154\ K + 39.154\ Cl = 2920.608$. From thirty equations of this kind the seven normals are constructed, each ratio contributing toward the establishment of each atomic weight represented in it. In this way errors of measurement are divided up and distributed, and even systematic errors find their influence diminished.

If all of the 30 ratios were equal in value and importance, the formation of the normals would be a comparatively simple matter, but such is not the case. Some are very exact, others are more than doubtful, and weight must be assigned accordingly. The rigorous rule is to give each measurement weight inversely proportional to the square of its probable error, and as the latter is given in every case, the rule has been applied. Only, instead of multiplying each equation by its weight, which would give coefficients of excessive size, I have divided them by suitable factors, and so reduced the coefficients to manageable dimensions. The principle is unchanged, but its mode of application is somewhat unusual. The same result, however, is reached in the end, and the element of personal judgment is entirely eliminated from the discussion. Each ratio weights itself, regardless of any preferences upon my part.

Now, taking the regular method of least squares, the thirty equations, after weighting, reduce to the following normals, seven equations containing the seven unknown quantities:—

1. $+5251.3245\ Ag - 6726.5755\ Cl - 599.0278\ Br - 143.1342\ I - 1238.429\ N - 1871.5887\ Na - 4417.7167\ K = 28800.227.$
2. $-6726.5755\ Ag + 12014.6535\ Cl - 24.7694\ Br - 2.8347\ I + 471.803\ N + 3146.9379\ Na + 6758.0443\ K = 41302.978.$

3. $-599.0278\ Ag - 24.7694\ Cl + 716.8553\ Br + 156.250\ N + 204.082\ Na + 27.72\ K = -230.712$
4. $-143.1342\ Ag - 2.8347\ Cl + 129.2642\ I + 0.5536\ K = 868.704.$
5. $-1238.429\ Ag + 471.803\ Cl + 156.250\ Br + 2954.376\ N - 35.1434\ Na - 334.7707\ K = -76872.85.$
6. $+1871.5887\ Ag + 3146.9379\ Cl + 204.082\ Br - 35.1434\ N + 3319.6292\ Na = 1919.906.$
7. $-4417.7167\ Ag + 6758.0443\ Cl + 27.72\ Br + 0.5536\ I - 334.7707\ N + 6748.573\ K = 24505.141.$

A glance at these equations is enough to indicate some of their deficiencies. The first two only are complete; in the others eight terms are missing. In the fourth equation, which represents iodine, the terms corresponding to sodium, bromine, and nitrogen are absent, and even potassium is represented by a coefficient which is ridiculously small. Many other coefficients are smaller than they should be, and this indicates the inadequacy of some of the data. To be really satisfactory, no one of the forty-nine coefficients should be wanting, and all should be reasonably large. Moreover, every coefficient should represent data drawn from more than one ratio, and in too many instances this is not the case. Were Stas's data alone considered, the normals would be still more incomplete, even though the outcome of the solution might be considered better.

Upon solving the seven normal equations the following values are obtained:—

Ag 107.9525.			
Cl	35.4521	N	14.0527
Br	79.9687	Na	23.0636
I	126.8663	K	39.1573

These, except in the case of chlorine, are considerably higher than than any of the values given in the table of reductions derived from the work of Stas, and yet they are not so inconsistent with the latter as they might appear to be at first sight. From the new atomic weights we can compute the value of each one of Stas's ratios, and so compare the result with the measurements which he actually made. This is done in the following table, which gives in each case the lowest and highest determination by the great Belgian:—

Ratio.	Stas.		Calculated.
	Lowest.	Highest.	
$KClO_3:O_3$	39.1527	39.162	39.149
$AgClO_3:O_3$	25.078	25.081	25.078
$AgBrO_3:O_3$	20.349	20.351	20.346
$AgIO_3:O_3$	16.972	16.9761	16.972
$Ag:Cl$	32.841	32.849	32.840
$Ag:Br$	74.079	74.083	74.078
$Ag:I$	117.529	117.543	117.520
$Ag:KCl$	69.099 (a)	69.1249	69.114
$Ag:KBr$	110.332	110.361	110.354
$Ag:NaCl$	54.2054	54.2093	54.205
$Ag:NaBr$	95.4383	95.4426	95.440
$Ag:NH_4Cl$	49.592	49.602	49.592
$Ag:NH_4Br$	90.823	90.8317	90.830
$Ag:AgNO_3$	157.463	157.510	157.481
$AgNO_3:KCl$	43.864	43.885	43.886
$KCl:KNO_3$	135.638	135.655	135.654
$NaCl:NaNO_3$	145.443	145.469	145.458

(a) Early work, supplanted by later and better measurements.

In ten cases out of the seventeen the calculated ratios fall within the limits of variation shown by the experiments of Stas; in six cases they are lower than his lowest, and in only one case is the result too high. In no case is the divergence large, and in most instances it is remarkably small. My conclusion from all of these considerations is, that although the new figures should not replace the accepted values for the several atomic weights, they are not to be lightly disregarded. They serve to exemplify the ultimate method of calculation, and to show that the data need reinforcement by additional determinations, which should complete the normals, and raise the weak coefficients to adequate magnitude. When that is done,

when, say, fifty ratios are available instead of thirty, then will the method of least squares be fully applicable to the problem, and its use will give the most probable results. To this end, ratios based upon analyses of sodium bromate, iodate, and iodide, potassium bromate and iodate, and ammonium iodide, are especially desirable. Other ratios connecting chlorine, bromine, and iodine with one another are also much needed, and should not be difficult to determine. For example, the ratio $\text{AgClO}_3 : \text{AgBr}$ ought to be easy of measurement, and also the reverse ratio $\text{AgBrO}_3 : \text{AgCl}$.

If the oxygen-hydrogen ratio be considered the base line in our system of atomic weights, then the determination of the seven constants now under consideration might be compared to a primary triangulation. For this purpose no accuracy is too high, no refinement of details too laborious. If the atomic weights of carbon and sulphur should be included in the scheme, giving 9 normal equations for solution, the range of possibilities would be much increased, and the results of the discussion could be made more satisfactory. With existing data, forty-four ratios, good and bad, are now available, and their distribution in the normals can be seen in the following table. Here each horizontal line represents the left-hand side of one equation, and each figure indicates the number of ratios which would influence a given coefficient:—

	Ag.	Cl.	Br.	I.	N.	Na.	K.	C.	S.
Ag ..	31	14	6	4	7	3	5	7	3
Cl ..	14	20	1	1	9	5	6	—	1
Br ..	6	1	7	—	1	1	2	—	—
I ..	4	1	—	5	—	—	2	—	—
N ..	7	9	1	—	13	2	3	1	—
Na ..	3	5	1	—	2	7	—	1	1
K ..	5	6	2	2	3	—	10	—	—
C ..	7	—	—	—	1	1	—	11	1
S ..	3	1	—	—	—	1	—	1	4

That is, the normal for silver would be formed from thirty-one ratios containing silver, fourteen containing chlorine, &c. The other equations would all be incomplete, twenty-four terms being absent, and eighteen more being affected only by single ratios. To supply the twenty-four and to improve the eighteen is the experimental part of the problem, and this is not so great a task as it might seem to be at a first glance. For example, suppose that the ratio $\text{AgCNS} : \text{AgI}$ were capable of measurement. Its errors of observation would be divided between five elements, eight missing coefficients would be supplied, and twenty-five coefficients in all would be affected. Merely to fill the gaps in the equations, therefore, is easy; to fill them properly is a more weighty question. To this end, forty or fifty new ratios ought to be carefully determined, giving a system of ratios containing from eighty to a hundred in all. For one chemist so great a labour would be hardly possible, but by co-operation between several workers the task might be performed, and in something like reasonable time. The methods of manipulation, the precautions to be observed, the difficulties to be encountered, are all well known, and that consideration helps to simplify the problem. Stas and Marignac have laid the foundations, and with their recorded experience to guide us we should be able to build the structure higher without excessive difficulty.—*American Chemical Journal*, xxvii., No. 5.

Direct Hydrogenation of Acetylenic Carbides by the Method of Contact.—Paul Sabatier and J. B. Senderens.—M. Moureu, who has lately made important syntheses from the two acetylenic carbides, heptene α and phenylacetylene, placed a quantity of these substances at the authors' disposal. To these they applied their method of hydrogenation. The details of the experiment show that copper enables the first stage of the transformation to take place with ease; that is, the passage into ethylenic carbides, but the second stage—that of transformation into formenic carbides—takes place much more slowly.—*Comptes Rendus*, cxxxv., No. 2.

COMMON ERRORS IN THE DETERMINATION OF SILICA.*

By W. F. HILLEBRAND.

To some it may seem as if a threadbare subject had been reopened in the above title, and that concerning a determination of such common occurrence in both technical and scientific operations little remained to be said or done. But that this is not so the following presentation will, I think, make sufficiently clear. Although not much of what I shall offer is really new, even that which is not will well bear repetition, having escaped the attention which it deserves. It seems to be advisable and necessary that public attention should be from time to time called to important facts which have not impressed themselves sufficiently to become a matter of common knowledge and application.

Regarding certain features of the silica determination I have long entertained doubts, but it is only very recently that convenient opportunity has presented itself for an investigation of these points as well as others, the direct incentive being afforded by an experience of the past summer as an outgrowth of the labours of a Committee of the New York Section of the Society of Chemical Industry having for its object the promotion of uniformity in technical analysis.

Uniform samples of raw cement mixture and of finished cement were sent to a large number of analysts for determination of the commoner constituents by the usual technical methods. The same samples were analysed in greater detail by myself and with the same regard to exactness that is usual in analysing rocks and minerals in the laboratory of the United States Geological Survey. Fourteen of the chemists besides myself returned reports, which showed in most cases a marked lack of agreement. The results for silica† only are here presented in tabular form with one exception, which is omitted for the reason that it does not profess to represent silica only, but rather the residue from evaporation of the limestone with acid, hence containing much undecomposed mineral matter.

TABLE I.—Silica Found by different Analysts in the same Samples of Raw Mixture and Finished Cement.

	Limestone mixture.		Finished cement.	
Standard ..	..	15.18	..	21.31
1 ..	..	15.75	..	20.90
1a ..	..	15.37	..	—
2 ..	..	14.68	..	20.92
3 ..	..	13.92	..	20.06
4 ..	..	—	..	20.00
5 ..	..	14.18	..	20.26
6 ..	..	14.70	..	20.96
7 ..	..	12.78	..	20.84
8 ..	..	13.97	..	19.82
9 ..	..	14.44	..	20.76
10 ..	..	13.60	..	19.18
11 ..	..	14.64	..	21.46
12 ..	..	14.18	..	20.76
13 ..	..	14.92	..	21.56
14 ..	..	13.56	..	19.53
Highest ..	..	15.75	..	21.56
Lowest ..	..	12.78	..	19.18
Difference ..	..	2.87	..	2.38

* Read at the Philadelphia Meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, vol. xxiv., No. 4.

† The full data, together with copies of the outlines of methods employed, were submitted to me for review and suggestion without knowledge on my part of the names of the analysts. My report was transmitted through the Director of the Geological Survey to the Committee of the New York Section of the Society of Chemical Industry, and its report was rendered at the Section Meeting on December 20, 1901, and published in the *Journ. Soc. Chem. Industry*, January 15, 1902.

Without detailing the various means employed for rendering silica insoluble, it may be said that all the workers strove to bring this about by the usual more or less approved methods of drying at temperatures ranging from that of the steam-bath for a long time to 120° and even higher for a shorter time. Despite their efforts there is not only a wide discordance in results, but, with two exceptions in each series, they are all too low. The actual failure to recover all silica is, however, in the majority of cases greater than the figures indicate, by reason of neglect of blast-ignition, or of correction by hydrofluoric acid, or both.

It is evident, then, that none of the methods in common use for rendering silica insoluble can be at all depended on to effect this result. None of the analysts except No. 1 and myself seems to have employed two evaporations with an intervening filtration. All others made but a single filtration, and in this simple difference lies the main solution of the trouble—a fact pointed out by Alex. Cameron with quantitative demonstrations nearly eight years ago (CHEMICAL NEWS, 1894, lxi., 171), but which has apparently almost escaped the notice of chemists. Indeed, I must admit a certain degree of remissness myself, for I have but an indistinct recollection that it was the reading of Cameron's paper when it first appeared which led me to adopt the practice of double evaporations with intervening filtrations which I have followed for a good many years. What influenced this change had escaped my mind until mention of Cameron's paper in a recent number of the *Journal of the American Chemical Society*, followed by its re-perusal, recalled the matter to recollection.

Other earlier writers, as Lindo, Craig, and Gilbert, have recognised the impossibility of recovering all silica by one evaporation, without, however, recommending a repetition after filtration. Instead, dehydration by hot sulphuric acid is often used in iron and steel works, but its use precludes satisfactory determination of other constituents in the same sample.

Cameron used in most of his experiments 2 grms. of silica, about 98½ per cent pure, fused this with 9 grms. of fusion mixture, dissolved the fused mass in hydrochloric acid, and evaporated in porcelain on the water-bath. The drying was continued on the water-bath in several experiments for some time after all acid fumes had ceased; in others, the dehydration was effected by the blue flame of an Argand burner. He found that, with the lower temperature, four—and even five—evaporations and filtrations were needed to reduce the silica recovered to a negligible quantity, but that with the higher heat three—or even sometimes two—sufficed. Furthermore, he showed by one experiment that a very common practice of evaporating several times to dryness with fresh portions of acid without intervening filtrations did not reduce the silica in the filtrate, and that the presence of aluminum, iron, and calcium was without influence on the results.

My own experiments to test all these points were entirely confirmatory of Cameron's, though less unfavourable as to the number of evaporations needed. This I attribute to the facts that I employed from one-half to one-fourth as much silica as he did, thus conforming more nearly to the ordinary conditions of a silicate analysis, and platinum instead of porcelain evaporating dishes. On the water- or steam-bath drying is not so speedily reached in porcelain as in platinum, and very possibly his later siliceous residues came in large part from the vessel itself.

The material employed in my tests was very nearly pure quartz crystal containing 99.88 per cent silica. Amounts of this lying usually within the limits 0.5 and 1 gm. were fused with 5 grms. sodium carbonate, the fused masses dissolved in hot water, then acidified by hydrochloric acid, and the solutions evaporated in platinum vessels for different lengths of time on a steam-bath. Then the residues were digested for a short time with hydrochloric acid and hot water. Prolonged digestion was unnecessary, as only

sodium chloride with mere traces of other salts had to be extracted.

TABLE II.—Silica Found in Filtrates.

	Weight of quartz.	SiO ₂ in first filtrate.	Per cent.	SiO ₂ in second filtrate.
1..	0.8943	0.0078	0.87	0.0012 (a)
2..	0.8208	0.0321	3.91	0.0006
3..	0.6401	0.0218	3.41	0.0005
4..	0.5738	0.0197	3.43	0.0009
5..	0.7028			0.6000
6..	0.5931	0.0167	2.82	0.0001
7..	0.7309	0.0211	2.89	0.0001
8..	0.8495	0.0204	2.40	—
9..	0.7841	0.0142	1.81	?
10..	0.7092	0.0089	1.25	0.0004 (d)
11..	0.7324	0.0247	0.64	0.0005
12..	2.0000	0.0193	0.96	0.0008 (e)

Remarks.

- Duration of first drying not known.
- Duration of first drying brief, not exceeding one to two hours, and in one case the residue still somewhat moist in parts.
- Duration of first and second drying twenty-one hours each. In 9 the mass was ground to powder as soon as free from visible moisture, without marked improvement in the result.
- Several evaporations with fresh acid before first filtration. Total duration of dryings and evaporations, twenty hours.
- Repeated (4) evaporations with water only before first filtration, twenty hours' drying before third filtration.

Experiment 10 was made in order to test the somewhat prevalent practice of evaporating several times with fresh acid before filtering. The result is an improvement over all but the first of the earlier ones, but still leaves much to be desired.

Experiments 11 and 12, in which repeated evaporations with water only were made, show a little better but by no means satisfactory result. The improvement in these last cases is not surprising, but it is to be expected that in ordinary analysis the foreign matter remaining with the silica would be increased by this treatment with water only instead of acid.

In order to learn, if possible, something about the effect of the large amount of sodium chloride in preventing the dehydration of silica, a soluble gelatinising zeolite (thomsonite with 41.17 per cent silica) was experimented with. The foreign chlorides in solution were here, of course, very much reduced in amount. The results are shown opposite 1, 2, 3 of Table III.

TABLE III.—Showing different Solubilities of the Silica Separated in Gelatinous and Granular Form from Zeolites.

	SiO ₂ in weight of zeolite taken.	SiO ₂ in first filtrate.	Per cent.	Duration of drying.
1..	0.4185	0.0065	1.55	2 hours.
2..	0.4142	0.0048	1.16	21 "
3..	0.8265	0.0072	0.87	21 "
4..	0.5736	0.0020	0.35	Brief.
5..	0.5760	0.0023	0.40	Prolonged.

Since the separation of silica from soluble silicates occurs in two forms, gelatinous and granular, according to the species acted on, it seemed worth while to try a non-gelatinising zeolite (heulandite) containing 57.18 per cent silica. The results appear opposite Nos. 4 and 5 of Table III. Manifestly the instantaneous separation of silica in granular form, without first entering into solution, is far more perfect than when it gelatinises.

We have thus seen how the serious errors in silica determinations shown by Table I. can be avoided by two evaporations with intervening filtrations. In extreme

cases a third evaporation may at times be advisable. Furthermore, that prolonged drying is a useless waste of time, except perhaps after the second evaporation, when, if results like 6, 7, and 8, of Table II, can be depended on, it may be of value in every exact work.

(To be continued).

THE POSSIBLE SIGNIFICANCE OF CHANGING ATOMIC VOLUME.*

By THEODORE WILLIAM RICHARDS.

COMPRESSIBILITY is a universal property of matter. It is so essential an attribute of the experimental universe that it is ascribed even to the imponderable and imaginary ether as well as to "material." The three states of matter are compressible in very varying degrees, dilute gases being compressible to a great extent, highly compressed gases and liquids to a far less extent, and solids to an extent usually even less than liquids. The first case has been studied in great detail, the last two scarcely at all.

Compressibility is simply an evidence of work done upon a system by a given pressure. If the application of considerable pressure in a system causes only a slight change of volume, it is evident that there must be other powerful influences at work. Clearly a clue as to the variation in these influences can be found in the quantitative study of the phenomena.

In all reversible cases which may be studied directly, an increase in pressure is accompanied by an increase of resistance to pressure and a diminution of volume. This depends upon the fundamental idea of equilibrium, and is a special case of the general principle sometimes named after Le Chatelier. Working backwards from this idea, one may infer with regard to any given substance at a given temperature, that it is under the influence of great pressure if its volume-change is unusually small under addition of a given pressure.

There are two conceivable causes of great compression in a substance. The pressure may be applied from the outside, or it may be due to the mutual internal attraction or affinity of the smallest particles of the substance for one another. That is, the substance may be compressed either by an outside pressure or by the intensity of its own cohesion. The first may be typified by highly compressed gases, the second by liquids, whose small compressibility may be taken as evidence of great compression.

In solids one must consider also the directive agency which manifests itself in crystalline form and optical structure. In a few cases the "crystallogenic force" seems to be rather directive than attractive; in other cases it seems to have both properties, for considerable diminution in volume may occur. The presence of the crystal-making force complicates the phenomena and is a considerable stumbling-block in the way of the study of the internal tension of solids.

In view of these facts, it seemed to me possible that the study of compression as manifested by atomic volume under different circumstances, as well as of atomic compressibility, might afford some light as to the affinities at work. The attempt, while only just begun, has not been wholly unsuccessful.

Evidently the liquid is the most suitable state in which to study the effects of molecular and atomic compressibility. It is most suitable because the irregularities in the behaviour of liquids are very great, indicating various internal stresses, and because they are nevertheless not at the mercy of the directive crystal-making tendency which superposes its own influence upon that of cohesion. The great difficulty in the subject lies in the fact that the total compressibility of a substance is usually made up of a

number of parts; the molecular compressibility might be due partly to a diminishing of the so-called "free space" between the molecules, as well as to a diminishing of the distance between the atomic centres. In words free from hypothesis, we may say that the compressibility may be made up of a chemical and a physical compressibility. When one comes to compute from compressibility the probable affinities, one is still more at a loss,—for each affinity is a mutual affair, concerning two specific substances. The immense number of variables thus introduced has discouraged most investigators, and I can find little if any hint of the significance of chemical compressibility in the literature familiar to me.

(The considerations of Nordenskjöld are too seriously complicated by uncertain assumptions to have much value. See Ostwald's "Lehrbuch," 1891, i., 850, for these and similar considerations).

In a case of this kind, one naturally seeks at first cases as simple as possible. A study of the volume changes which take place on mixing liquids reveals at first no apparent regularity. In some cases an expansion occurs, but more usually a contraction; sometimes heat is evolved, and at other times heat is absorbed. One law may, I think, be detected in the midst of the confusion, namely, *similar liquids exhibit less change of volume on mixing than dissimilar ones do*; that is, where the affinity of a substance for itself is not unlike that of the substance for another, no great contraction or expansion occurs on mixing. Thus benzol and toluol when mixed scarcely change in volume at all, while alcohol and water contract considerably. That is just what would be expected if affinity is the cause of contraction.

In order to use such facts it is not necessary to imagine an atomic theory adapted to them. Such a theory is ventured upon at the end of this paper, but the facts are significant without it. One only has to bear in mind that liquid and solid substances resist compression, and hence that when we find them compressed we have reason to believe that pressure has been applied upon them. It is rather a matter of common sense than a hypothetical abstract conception.

In order to present in a clear light the complications involved in the study of even a simple series of cases of chemical compression, the facts concerning the molecular volumes of several metals and their oxides are recorded and discussed below.

Molecular Volumes of Oxides.

Sub-stance.	Weight of metal combined with 16 grms. oxygen.	Density of metal.	Density of oxide.	Space occupied by given weight of metal.	Space occupied by corresponding weight of oxide.	Excess of volume of oxide.
2Ag ..	215.86	10.56	7.521	20.55	31.55	+11.00
Hg ..	200.00	13.59	11.136	14.71	19.4	+4.7
Cu ..	63.6	8.95	6.40	7.10	12.4	+5.3
Ni ..	58.7	8.9	6.39	6.60	11.75	+5.15
Cd ..	112.3	8.67	6.5	12.95	19.7	+6.75
Zn ..	65.4	6.9	5.6	9.5	14.5	+5.0
Mg ..	24.36	1.74	3.4	14.0	12.0	-2.0
2Na ..	46.1	0.973	2.80	47.4	22.6	-24.8
2H ..	2.0	0.07	1.00	28.2	18.0	-10.0
Si ..	14.2	2.00	2.30	7.1	13.14	+6.0

In compounds of carbon, according to position 4.7 to 12.0

In liquid oxygen at -119° and 50 atmospheres (sp. gr. = 0.65) O = 24.5 c.c.

In liquid oxygen at -183° and 1 atmosphere O = 14.1 c.c.

While in the first part of this paper no atomic hypothesis is assumed, the words atomic volume, atomic weight, and atomic heat will be used in a purely material sense, as the actual constants pertaining to quantities chemically consistent.

The results recorded in this table are typical of the variety of degrees of contraction which take place when sub-

* From the *Proceedings of the American Academy of Arts and Sciences*, xxxvii., No. 1.

stances combine with oxygen. It is evident that in some cases the product occupies considerably more space than the metal from which it was formed, and that in others (typified by magnesium and sodium above) the oxide occupies considerably less space than the metal. This last remarkable circumstance at once emphasises the absurdity of estimating the atomic volume of an element in a compound by discovering the volume-change which takes place when that element is replaced by another. Oxygen cannot be said to occupy a *minus* quantity of space—the only possible outcome of the false assumption in this particular case. The false method gives fairly consistent results among carbon compounds only because of the great similarity of their composition. This consideration leads to the first law underlying the change of volume in chemical or physical change, namely, *the atomic volume is not a constant, but is dependent upon the environment*. This law was first suggested by Horstmann ("Ostwald's Lehrbuch," 1891, I., 389), but he looked upon it rather as the absence of a law than as the presence of one.

If the affinity of oxygen for the metal were the only variable entering into the figures given above, it is obvious that the total contraction, the difference between the volumes of factors and product, would be at once a comparative measure of the attractive forces which produce the compression. This reasoning of course rests upon the plausible ground that a state of being which resists pressure, such as liquid oxygen or solid metal, may be compressed only by the application of pressure. In this case pressure may be supposed to be applied by the mutual affinity. But unfortunately the case is not so simple.

It is clear that in each case recorded above at least three affinities are concerned; first, the affinity of the metal for itself; second, the affinity of oxygen for itself; and third, affinity of the metal for oxygen. The second of these is constant throughout the series, hence for the present comparison it may be considered as a known quantity. Therefore each change of volume may concern at least two unknown quantities. Hence if it were possible to measure either of the two variable affinities, an approximate idea could be obtained concerning the other from these data concerning atomic and molecular volume.

A slight uncertainty is caused also by the possible varying intensity of the "crystal-making tendency" which determines the structure of solids. The small differences caused by this uncertainty may be seen from the following typical calculation. If solid rather than liquid mercury had been chosen above, the atomic volume of the mercury would have become $\frac{200}{14.1} = 14.2$ instead of

14.7, and the excess of volume of the oxide would have been 5.2 instead of 4.7. These differences are unimportant compared with the larger values under consideration; the precise state of the solids or liquids makes less difference than one would have supposed.

Is there any direct method of determining either the mutual affinity of the two elements or the affinity of the metal for itself?

Countless attempts to measure the former have so continually resulted in failure that many chemists are inclined to deny the existence of chemical affinity. The electro-metric method suggested by Ostwald ("The Chemo-meter," *Zeit. Phys. Chem.*, 1894, xv., 399) clearly measures one of the ways in which chemical affinity may accomplish work, but it is limited in application and only represents a small fraction of the possibilities. The thermal relations are complicated by well-known thermodynamic irregularities, and would be fully significant only at the imaginary absolute zero.

The direct determination of the affinity of a substance for itself is an easier matter, for many of the properties of a single substance, such as volume, compressibility, tenacity, must be associated with this affinity. Let us seek to study these relationships more closely.

If one could only be sure that all substances, when re-

lieved of their self-affinity, would occupy the same volume, the atomic volume itself would be the simplest and most direct means of comparing this property in different substances. The smaller the actual atomic volume, the greater must be the self-affinity. Such an assumption would at first sight seem to be justified, for those elements which have the largest atomic volumes have the least inclination to remain in the elementary states. Deserting the elementary state means introducing other affinities, however; hence the assumption would be unsafe.

It has been already pointed out that compressibility, if measured over a wide range of pressures, might afford a clue to the extent of compression already existing in any given substance. But the comparison of different substances involves the dangerous assumption that all substances would be alike compressible if freed from self-affinity—an assumption which seems more probable than the last, but which nevertheless must be rejected. A much safer measure of the stress under which a single substance rests is the work which heat is able to do upon it. The changing of a simple substance from t° to $t^\circ + dt^\circ$ centigrade must involve the addition to it of an amount of internal work which is represented by the rise of temperature multiplied by the heat capacity of the substance, or $C dt$. In a simple elementary substance, when this work does not involve the alteration of crystalline form or any other apparent change except increase in size, it seems reasonable to consider no other variables, at least as a working hypothesis. If this is the case, we may write $C dt = P dv$, in which P is the internal stress against which the heat-energy is doing work, C the molecular heat capacity, t temperature, and v volume. The stress against which this work is being done is due only to the internal stress and to atmospheric pressure (which latter may be neglected by comparison with the very large value of the former), hence the stress $= P = \frac{C dt}{dv}$. This can apply

precisely only to infinitesimal changes, because in all probability P will vary with the volume. While it cannot be claimed that the expression just given certainly expresses a single pressure pitted against temperature-work, the expression certainly represents a resultant tendency which opposes expansion by heat, and therefore, by inference, opposes all other forms of expansion.* It is the *inward tendency*, the opposite to the driving tendency (Richards, *Proc. Amer. Acad. Arts Sci.*, xxxv., 471) or fugacity (Lewis).

While then this stress, represented by the quotient of energy divided by change of volume, can hardly represent anything very definite, it must nevertheless be supposed in a general way to increase when the self-affinity increases. Hence, while giving no certain knowledge, its study may give an indication of affinity.

A typical comparison may be made of the two elements zinc and mercury. They are simple, similar, and yet widely different as to their power of holding oxygen. In each case the atomic contraction on union with oxygen is about the same; If we take as the atomic volume of oxygen the atomic critical volume, the contractions are as follows:— $14.7 + 24.5 - 19.4 = 19.8$, in the case of mercury, and $9.5 + 24.5 - 14.5 = 19.5$, in the case of zinc. If the metals were originally subject to the same internal stress, we should infer from the similarity of contractions that the affinities concerned in the two cases were about equal. This inference is, however, overthrown by other facts. Both elements have about the same atomic heat capacity, hence no internal rearrangement takes place in one which is not approximated in the other. On the other hand, the increase in atomic volume for a rise of 1° of temperature exhibited by one is much greater than that exhibited by the other.

If a grm. atom of one element increases more rapidly in size than the grm. atom of another, it is only reasonable

* All the aught data which we possess upon compressibility seem to run parallel with the coefficients of expansion.

to suppose that the heat energy is finding less opposition in the former case. The coefficient of cubic expansion of mercury is 0.000179 at 0° C. and the heat required to raise a grm. through 1° is 0.139 Joule. With zinc the corresponding numbers are 0.000087 and 0.392.* The respective atomic volumes are 14.7 and 9.5. Substituting these values in the equation we obtain:—

$$P_{Hg} = \frac{(200 \times 0.139)}{(14.7 \times 0.000179)} = 106,000 \text{ megadynes per sq. cm.}$$

$$P_{Zn} = \frac{(65.4 \times 0.392)}{(9.5 \times 0.000087)} = 310,000 \text{ megadynes per sq. cm.}$$

Both these pressures are very large, for a megadyne exert on a square centimetre a pressure of almost an atmosphere. As has been said, they signify a resultant tendency which resists expansion.

It is interesting to note that these stresses agree in their indications with the comparison of boiling-points and latent heats of evaporation. The boiling-point of mercury is 357° C. and that of zinc about 930° C. The latent heat of evaporation of zinc is not known, but there is no reason for believing that in its case Trouton's rule is broken. Hence the criteria all indicate that zinc is harder to dissociate from itself than mercury is.

A comparison of the energy-quotients of several metals, measured in this way, may be of interest.

Metal (in order of boiling-point).	Boiling-point, 760 m.m.	Heat capacity (mayers per grm.)	Cubic coeff. of expansion.	Energy quotient
		C = mol. wt.		$P = \frac{Cdt}{\text{at. expn. megadynes.}}$
Mercury..	357° C. = 630° A.	0.139	0.00018	106,000
Cadmium..	770° C. = 1043° A.	0.23	0.000093	214,000
Sodium ..	860° C. = 1133° A.	1.21	0.00022	53,700
Zinc ..	930° C. = 1203° A.	0.392	0.000087	310,000
Copper ..	Unknown	0.375	0.00050	672,000
Magnesium	1100° ± 1400° A.	1.02	0.000081	224,000
Lead ..	1400° ± 1700° A.	0.126	0.000088	162,000
Silicon ..	Unknown	0.7	0.0000230	755,000
Diamond.	Unknown	0.5	0.0000036	4,900,000

In these figures one may find traces of many properties associated with firmness of structure or intensity of self-affinity. For example, the order of sequence of the energy-quotients agrees essentially with that of tenacity and of hardness. There is some relationship also to boiling-points and melting-points, although here there are more exceptions. "Chemical affinity" is so much affected by electrical relations and by atomic volume that one would expect to find regularity only on comparing similar elements. Such comparison (zinc with cadmium, or carbon with silicon) seems to show that the energy-quotient tends to increase with diminishing atomic weight.

(To be continued).

NOTICES OF BOOKS.

Catalogue of Scientific Papers (1800-1883), Supplementary Volume. Compiled by the Royal Society of London. Volume XII. London: C. J. Clay and Sons. 1902. Pp. 807.

AFTER a careful sifting of a preliminary list of periodicals not previously catalogued it was found that upwards of three hundred and fifty serials remained to be dealt with. A list of these, many of which were by no means easy of access, together with the abbreviated references adopted, is prefixed to this volume. A few modifications have been introduced in the method of compilation, which cause the present volume to vary in some respects from those previously issued. Numerous cross references have been given, so that it is hoped no difficulty will arise in discovering the works of any Russian or other author.

* All figures not otherwise designated were taken from the tables of Landolt and Börnstein, 1894.

The New Volumes of the Encyclopædia Britannica. The Fourth of the New Volumes, being Vol. XXVII. of the Complete Work. London: *The Times*. Edinburgh: Adam and Charles Black. 1902. Pp. 742.

THE fourth of the new volumes commences with an important series of articles on electricity and electrical matters in general. Prof. J. A. Fleming contributes five, viz., "Electrical Conduction," "General Principles," "Lighting," "Electric Current and Electric Units," and "Electro-Magnets"; Mr. W. G. McMillan writes on "Electro-Chemistry and Electro-Metallurgy"; Mr. W. C. D. Whetham on "Electrolytic Conduction"; and Prof. J. J. Thomson on "Electric Discharge and Electric Waves."

Prof. H. L. Callendar contributes an article on "Fusion," and Prof. Lunge a very interesting one on "Gaseous Fuel." Natural gas is of importance in some of the States of North America, but the author considers artificial gas of much more general importance. The principle classes of gaseous fuel, as classified in this article, are coal-gas, coke-oven gas, producer gas, Siemens gas, blast-furnace gases, water-gas, semi-water-gas, of which a modification is the Mond gas, and air-gas, which is produced by forcing air through volatile inflammable liquids.

The article on "Artificial Gems," by Sir William Crookes, is of interest; in it the writer describes the artificial production of diamonds, the largest of which, however, has only reached a diameter of 0.5 m.m. The artificial ruby is also described; this substance was first made in a practical manner by MM. Frey and Feil in 1877, while in later years, Elsner, De Senarmont, Deville, and Caron and Debray have produced these gems with more or less success. Sir W. Roberts-Austen has also recently produced rubies as a by-product in the manufacture of metallic chromium. Other gems which have been produced by artificial means are the sapphire, the Oriental emerald, the Oriental amethyst, the Oriental topaz, and the zircon.

Metallography, an Introduction to the Study of the Structure of Metals, Chiefly by the Aid of the Microscope. By ARTHUR H. HIGGINS, Head of Metallurgical Department, Birmingham Municipal Technical School. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1902. Pp. 158.

AS metallography is as yet only in its infancy and is not sufficiently developed to permit of its being placed on a strictly logical scientific basis, the author only claims to have made an attempt to lay the principles of the subject before students and workers who are interested in the properties and applications of metals, and to offer a series of original illustrations which it is hoped will assist in making the meaning clearer.

The introductory chapter gives a brief account of the history and development of metallography, including a statement of the nature of alloys as generally recognised by eminent metallurgists, apart from microscopic considerations. An alloy may be compared to a rock which contains different constituents, all of which may be united in the liquid condition, but separate on cooling, forming two or more alloys of different densities and of different fusibilities. Or many solid alloys, when heated, release certain of their constituents that have different freezing-points from the remainder. In fact, a cooling mass of metals often behaves like water containing suspended matter does in freezing, when the ice first formed rejects the foreign matter; and so the portion of the alloy which first solidifies rejects certain other portions of the constituent metals.

Polishing the metal is a matter of great importance for the exact examination of the structure of metals, and the chapter dealing with this subject should be carefully studied. Etching and tinting are also matters of considerable interest, as it is through this means that the structure of the metals is made visible.

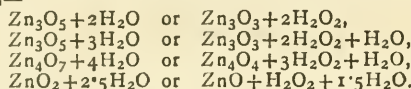
The bulk of the book, beginning with Chapter IV., on the "Structure of Iron," deals with the structure of a large number of metals and alloys, and the letterpress is amplified by 96 excellent microphotographs which are deserving of much praise. A glossary of technical terms is to be found on page 149 and following, while a fairly good index completes the volume.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

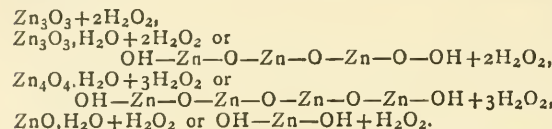
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 2, July 15, 1902.

Preparation and Properties of a Vanadium Silicide.—H. Moissan and M. Holt.—To prepare the compound VSi_2 the authors heated a mixture of vanadic oxide, V_2O_5 , with slightly over five times its weight of pure crystalline silicon in the electric furnace. The reaction takes place according to the equation $2\text{V}_2\text{O}_5 + 11\text{Si} = 4\text{VSi}_2 + 3\text{SiO}_2$. The same silicide can also be prepared by the reduction of a mixture of silicon and vanadic acid by magnesium powder. Vanadium silicide, as prepared by either of these methods, is in the form of brilliant metallic prisms. It has a density of 4.42, and is fusible and volatile in the electric furnace. An analysis of this substance shows it to have the formula VSi_2 .

Properties and Constitution of Zinc Peroxides.—M. de Forcrand.—The author, in a previous paper, described four zinc oxides, which, according to their methods of preparation, appeared to be the definite compounds—



After a series of further experiments on these four substances, he believes them to have the constitutional formulæ—



The oxides $\text{Zn}_3\text{O}_3, \text{H}_2\text{O}$ and $\text{Zn}_4\text{O}_4, \text{H}_2\text{O}$ being polyzincic or metazincic acids of the same nature as hydrates of condensed oxides and analogous to the hydrated sulphides $\text{Zn}_3\text{S}_3, \text{H}_2\text{O}$ and $\text{Zn}_4\text{S}_4, \text{H}_2\text{O}$. This constitution can be compared to that of perchromic acid, which has the constitution $\text{CrO}_3, \text{H}_2\text{O}_2$, according to Moissan, or $\text{Cr}_2\text{O}_7, 2\text{H}_2\text{O}, \text{H}_2\text{O}_2$, according to Berthelot. In all cases the hydrated peroxides of zinc are very different from the hydrated peroxides of calcium, barium, lithium, and sodium.

Oxyisopropylphosphinic Acid.—C. Marie.—The formulæ of the salts and the ethers and the existence of a benzoyl derivative justifies the name oxyisopropylphosphinic acid, and gives a means of establishing its formula, $(\text{CH}_3)_2\text{C}=\text{O}-\text{OH}$

This is the first body of a new series of oxyphosphinic acids which can be compared with the oxyphosphinic acids prepared by the action of PCl_3 on the fatty or aromatic aldehydes.

New Method of Preparation of Substituted β -Ketonic- α -substituted Ethers.—René Locquin.—When the chlorides of the fatty acids act on sodium acetylacetic ethers, a mixture of the two isomeric acyl-derivatives is obtained. The C-acetylacetates, $\text{CH}_3-\text{CO}-\text{R}-\text{CO} > \text{CH}-\text{CO}_2\text{R}'$, when treated with aqueous potash or gaseous ammonia, gives a series of acetylacetates, $\text{R}-\text{CO}-\text{CH}=\text{CH}-\text{CO}_2\text{R}'$, possessing properties analogous to those of the acetylacetates, and, amongst other properties, that of replacing one of the hydrogen

atoms of the CH_2 group by a radicle, R' , when treated with a mixture of sodium ethylate and alcoholic iodide, RI .

MISCELLANEOUS.

Institute of Chemistry of Great Britain and Ireland.—The next Examination in the Branch of Biological Chemistry will be held at the Laboratories of the Institute, 30, Bloomsbury Square, London, W.C., on Tuesday October 21, 1902, and three following days. The Examination will extend over four days, and the syllabus will include Biological Chemistry, with special reference to the Chemistry and Bacteriology of Foods, Water, Sewage, and Effluents, and the practical applications of Biological Chemistry to Industries. Examinations in the Branch of Biological Chemistry of the Final Examination are held annually in October. The Examinations in the other Branches are held in January and July. Candidates intending to enter for the Final Examination in the Branch of Biological Chemistry are recommended to take (after passing the Intermediate Examination, or any Examination qualifying for admission to the Final) a course of study covering the following work:—A course of forty to fifty Lectures on the Morphology and Physiology of Micro-organisms. Practical work to include—(a) Microscopy, the preparation, staining, mounting, drawing, and recognition of specimens; (b) the preparation and study of pure cultures; (c) the conduct of fermentation experiments, and the study of chemical changes brought about by bacteria, moulds, yeast, &c.

New Volumetric Estimation of Bromides in the presence of Chlorides and Iodides.—Von Weszelsky.—Acid chlorine water transforms iodides into iodates and displaces the bromine from bromides, no matter what excess of chlorine is used. In alkaline solution the bromides are transformed into bromates by an excess of chlorine water. On these facts the author has based the following method of estimation:—If the substance does not contain iodine, about 1 gm. of carbonate of potassium and the corresponding quantity of chlorine water are added to the solution; it is then evaporated to dryness. The residue, dissolved in 100–150 c.c. of water, is acidulated and titrated by hyposulphite of soda after the addition of a little iodide of potassium. If the solution contains both bromine and iodine it is placed in a retort, acidulated, and after adding chlorine water in sufficient quantity to oxidise the iodides to iodates and displace the bromine from the bromides, it is distilled in a current of carbonic acid. The bromine and the excess of chlorine are collected in an aqueous solution of 1 gm. of potash; after the potash is completely saturated by the carbonic acid it is evaporated to dryness, and taken up with water and iodide of potassium to titrate, by means of hyposulphite, the iodine displaced by the bromate. Chlorates in small quantities have no action on the iodide of potassium, but iron, arsenic, and antimony ought first to be eliminated in the ordinary way. This method applied to the analysis of mineral waters has given very concordant results.—*Zeit. Anal. Ch.*, vol. xxxix., p. 81.

NORTHERN POLYTECHNIC INSTITUTE, HOLLOWAY, LONDON, N.

The Governors of the above Institute invite applications for the Post of HEAD of CHEMICAL DEPARTMENT. Salary £250 per annum for whole time service. Duties to commence on Sept. 18th, or as soon after as possible. Applications to be sent in by Sept. 3rd on special forms to be obtained from—
W. M. MACBETH,
Clerk to Governors.

August 12, 1902.

THE SOUTH-WESTERN POLYTECHNIC, CHELSEA, S.W.

The Governing Body invite applications for the DEMONSTRATORSHIPS of CHEMISTRY and PHYSICS and the LECTURESHIP of MATHEMATICS. The remuneration attached to each of the three posts is £150 per annum. Candidates must apply on or before Sept. 2nd. Particulars of duties and forms of application may be obtained from the SECRETARY.

THE CHEMICAL NEWS.

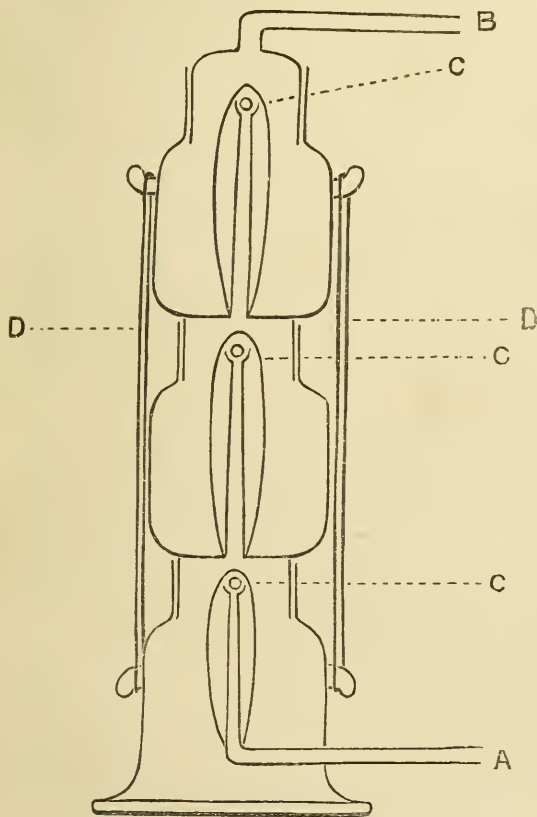
VOL. LXXXVI., No. 2230.

A TRIPPLICATE APPARATUS FOR DRYING AND PURIFYING GASES.

By EDWIN DOWZARD, F.C.S.

THE accompanying sketch is that of an apparatus for drying and purifying gases.

The special point about this apparatus is that three different reagents, either solid or liquid, may be used. For example, the bottom cell may contain a strong solution of KHO, the second cell H_2SO_4 , and the third, soda-



A, Inlet; B, outlet; C, C, C, ball valves; D, D, elastic bands connecting top and bottom cells.

(The above sketch is half actual size).

lime. When solids are used, a small quantity of glass-wool should be placed on the floor of cell so as to cover the inlets.

This apparatus is recommended for organic analysis, as it is very efficient, occupies little space, and is easily cleaned and filled. A battery of two triplicate washers is sufficient for all ordinary purposes. The working capacity of each cell is about 45 c.c.

The above apparatus is made by Messrs Gallenkamp and Co., 19, Sun Street, London.

SOLANUM DULCAMARA.

By FREDERICK DAVIS.

THE *Pharmaceutical Journal* of October 23, 1886, contains the following Editorial Note:—

"Some uncertainty prevails as to whether the fruit of *Solanum dulcamara* is poisonous, and the question having been raised in *Science Gossip* last month Mr. F. Davis has made some experiments on the point, from the results of which it appears that the fruit contains an alkaloid similar to that obtainable from belladonna. Mr. Davis has found that this alkaloid has the power of dilating the pupil of the eye, and he considers that it may be intermediate in character between atropine and physostigmine. The ripe berries yield a larger amount than those which are unripe."

Since the above note appeared I have at various times engaged myself in the further examination of this plant, operating for the most part upon fresh specimens collected upon the Surrey Hills and growing, of course, upon chalk and bed of gravel.

The methods employed were those indicated in Dragendorff's plant analysis.

The substances separated were:—

- | | | |
|----------------|-------------|------------------|
| (a) Solanine | } | Alkaloids |
| (b) Solanidine | | |
| (c) Solanein | | Glucoside |
| (d) Dulcamarin | | Bitter principle |

The solanine was removed from its salts in aqueous solution by amyl alcohol, finally crystallising in four-sided prisms having a melting-point $235^{\circ}C$.

The taste is bitter, with subsequent burning sensation to the tongue and back of the mouth.

The alkaloid gave an alkaline reaction with litmus.

Solanine does not appear to be soluble in water except very sparingly, but the sulphate, hydrochloride, and bimalate are freely soluble; indeed, the alkaloid exists in the ripe fruit as bimalate.

The bulk of the acid of the fruit was proved to be monohydroxy-succinic acid.

The percentage found in the ripe fruits in ten separate determinations varied between 0.3 and 0.7.

Reactions for solanine as found are as follows:—

Phospho-molybdic Acid.—Canary-coloured precipitate.

Potassio-bismuthic Iodide.—Red precipitate.

Froehde's Reagent.—Red, becoming brown, finally yellow.

Concentrated Sulphuric Acid.—Ruddy yellow.

Alcohol and Sulphuric Acid.—Red when warmed.

Does not reduce Fehling's solution.

Solanidine.—This alkaloid was found chiefly in the leaves and young shoots, but it also exists in the fruits; in fact, it would appear that solanidine is the prior alkaloidal product, and that solanine is, as it were, the ultimate product of the plant. Solanidine is soluble in alcohol, whereas solanine is practically insoluble excepting in boiling alcohol of specific gravity 0.840. The salts of solanidine are slightly soluble in water.

Solanidine was removed by chloroform from an alcoholic extract of the plant.

It crystallises in brilliant acicular form, has a bitter and acid taste, and a melting-point $205^{\circ}C$.

Hydroxide of potassium, sodium, or ammonia precipitate solanidine as a gelatinous mass.

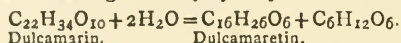
Solanein.—Some little trouble was experienced with this substance found in the alcoholic extract with the solanidine, it finally remaining as a non-crystallisable body, horny in character, and of a yellow colour. Solanein is a glucoside, and has a melting-point $208^{\circ}C$. When boiled with very dilute hydrogen sulphate or hydrogen chloride it breaks up into solanidine and grape-sugar. Solanein reduces Fehling's solution.

Dulcamarin.—This substance exists throughout, as evidenced by exhausting the root, stems, leaves, and fruit

separately with acetic ether, then precipitating with basic lead acetate.

It is at first taste intensely bitter, gradually giving place to a sweet and not unpleasant flavour; in fact, exactly the reverse to that which the name would imply. It does not answer the general tests for alkaloids, but dissolves in alkaline hydroxide with a ruddy brown colouration.

Dulcamarin gives a rose-pink colour with concentrated hydrogen sulphate. It is readily soluble in alcohol, and by boiling with dilute hydrogen sulphate is broken up into dulcamaretin and glucose by hydrolysis as follows:—



Dulcamarin.

Dulcamaretin.

I find upon referring to the literature upon *Solanum dulcamara* that all authorities speak of dulcamarin, and appear to consider that this bitter principle is the active agent in this plant, some even stating it to be an alkaloid, which, however, it certainly is not, yielding none of the characteristic reactions of these bodies; neither does it form salts with dilute mineral acid. If, however, it be boiled with dilute hydrogen sulphate or hydrogen chloride grape-sugar is produced, and Fehling's solution may be reduced by the results; it is therefore a glucoside as well as a bitter principle.

Some diversity appears to exist respecting the formula of solanine. Firbas gives $\text{C}_{52}\text{H}_{92}\text{NO}_{18}$, whilst Hilger is of opinion $\text{C}_{42}\text{H}_{75}\text{NO}_{15}$ represents it.

Personally, I find the formula to approximate the latter; three separate workings giving by average $\text{C}_{42}\text{H}_{75}\text{NO}_{12}$.

Solanidine is said by Hilger to possess the formula $\text{C}_{25}\text{H}_{44}\text{NO}_2$, Firbas giving $\text{C}_{40}\text{H}_{61}\text{NO}_2$.

Three separate determinations of my own yielded an average $\text{C}_{41}\text{H}_{71}\text{NO}_2$.

Solanine.—Firbas gives the formula of this substance as $\text{C}_{53}\text{H}_{83}\text{NO}_{13}$.

After repeated experiments I cannot agree with this statement, this glucoside giving in my hands $\text{C}_{48}\text{H}_{78}\text{NO}_{13}$. In any case this glucoside contains nitrogen.

After these researches had been completed a sample of solanine was obtained from a well-known German firm and compared with that obtained from the fresh plants as previously indicated; it was found that in taking the melting-point, which approximated 235°C , a sublimate occurred in acicular crystals. Subsequent treatment proved these crystals to be solanidine; it seems, therefore, that commercial solanine is a mixture of solanine and solanidine.

THE DETERMINATION OF COPPER BY ALUMINUM FOIL.*

By GEORGE E. PERKINS.

THE following method is a modification of the process by A. H. Low. The copper is brought into solution as a sulphate by treatment similar to that in Low's modified cyanide process. The solution is evaporated until all nitric acid has been driven off and dense white fumes appear. Water is added until the dilution is about 50 c.c. of water to 10 c.c. of sulphuric acid. Sheet aluminum of about 25 gauge thickness is cut into pieces about 40 m.m. square with one corner of each piece turned up for convenience in handling. Two or three of these pieces are added to the beaker containing the solution of copper. The solution is then boiled. In about five minutes, all of the copper is precipitated upon the aluminum sheets.

Instead of re-dissolving the deposited copper and titrating with cyanide solution, more satisfactory results are obtained by washing the deposited copper into a tared

Gooch crucible, by giving a final wash with alcohol, and by burning off the alcohol and drying. Weigh the result as metallic copper.

In forming the filter, care should be taken that only sufficient asbestos fibre is used to produce a good filter. In washing with alcohol and burning, the same care is needed as in the electrolytic method that too much alcohol is not used.

THE CLASSIFICATION OF THE ELEMENTS.*

By HENRY E. ARMSTRONG, V.P.R.S.

ALTHOUGH no direct evidence acceptable to chemists has been adduced which in any way justifies the belief that the elements are decomposable, it is impossible to resist the conclusion that they are genetically related—so closely in many respects do they resemble a series of related compounds, especially when regarded from the point of view of the organic chemist. The generalisation known as the *Periodic Law* is in itself a justification of this view; the manner in which interrelationship becomes manifest when they are classified in accordance with its canons, being probably the strongest of all the arguments which can be cited as tending to show that the elements are compounds—but compounds very different from those with which we are accustomed to deal. Even in the form in which it was put forward by Mendeleeff, however, the periodic generalisation is but a first approximation; and the great Russian has himself pointed out that it needs improvement and development (Faraday Lecture, *Trans. Chem. Soc.*, 1889, p. 656). As chemists are beginning to recognise this (compare Biltz, *Ber. Deut. Chem. Ges.*, 1892, p. 562), I venture to submit a scheme of classification which I have been led to draw up in writing an article for the Supplement to the "Encyclopædia Britannica." This article, I may say, was sent to press in May, 1900, and the first proof before me is dated November 20, 1900.

The suggestion of an octave of elements having been made in early days, the tendency to adopt an octave system has been irresistible. It is difficult now to discover any real justification of such a practice. As there frequently a difference of (about) a single unit between the atomic weights of contiguous elements, and as the "homologous" elements among those of lower atomic weight differ by (about) sixteen units—I assume that the "elementary difference" may be (about) a single unit, and that the first "horizontal period" comes to an end with oxygen; in other words, that there are sixteen "vertical series" of homologous elements.

In Table I, the elements are entered under whole numbers without regard to their exact atomic weights. The dominant principle on which the arrangement is based is that of maintaining elements which belong to the same family in the appropriate columns. The chemist cannot adopt any other mode of arrangement in view of the uncertainty which attaches to many of the atomic weights.

I have not hesitated to assume that the molecules of argon and similar elements are polyatomic like those of nitrogen—their nearest ally in outward behaviour—and have regarded them as *diatomic*, as the molecules of all the ordinarily gaseous elements are of this order of complexity. It has always been my opinion that they are elements of intense activity, the atoms of which so fully satisfy each other that no residual affinity is manifest in the molecules. From this point of view the appearance of argon immediately after fluorine is quite in order.

Turning to the several periods, the first calls for little remark. Helium is put next to hydrogen—and it may well be that elements somewhat like helium and argon will

* Read before the January meeting of the Rhode Island Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxiv, No. 5.

* A Paper read before the Royal Society, March 20, 1902.

[illegible]

be discovered which will fall into positions 3, 4, and 18; in fact, this region may well turn out to be the nesting-place of such elements. Beryllium is shown separated from lithium and magnesium, but not to an extent which need give rise to objection. It is perhaps not beyond the region of possibility, however, even in the case of an element with so low an atomic weight, that isomorphous mixtures may have passed as pure substances; this possibility has not been sufficiently taken into account in preparing the material for determinations of atomic weight.

In the second period, although it does not come immediately below nitrogen, phosphorus is very near to that element—and sufficiently so to correspond with their very close relationship.

In the third period, when scandium is passed, it is impossible to proceed by units; to bring titanium into position it is necessary to step down five units. Proceeding from titanium, however, vanadium and chromium fall into appropriate positions.

In the fourth period, a similar step down in the fourth column from iron to cobalt and nickel is necessary to bring copper into an appropriate position; and for a like reason zinc is included in a group with copper. There are similar drops in the eleventh and twelfth columns. Selenium appears with 77 instead of 79 as its atomic weight, in order to preserve it in the oxygen-sulphur series; bearing in mind that the atomic weight of sulphur differs from that of chlorine by fully three units, whereas that of selenium is ordinarily supposed to differ from that of bromine by only a single unit, the change does not appear to be an unjustifiable one.

The same argument applies to tellurium in the following period. Personally, I entertain no doubt that the atomic weight of this element will ultimately prove to be considerably lower than that of iodine.

(To be continued).

THE RATIOS OF THE ATOMIC WEIGHTS.*

BY ARTHUR MARSHALL, F.I.C., F.C.S.

MANY remarkable relationships have been noticed between the atomic weights of the elements, but in working them out it has been usual to always refer the atomic weights to that of hydrogen as unity, or that of oxygen as 16. In the following note, after calling attention to some of the relationships that are noticeable under these circumstances, I shall point out some regularities which appear when the atomic weights are referred to entirely different standards.

Since the time of Prout numerous chemists have been struck by the fact that many of the atomic weights approach very closely to whole numbers. This tendency is more pronounced when they are referred to $O = 16$ than when referred to $H = 1$. Strutt, in a recent paper (*Phil. Mag.*, 1901, vi., 311), has calculated the probability of the best known atomic weights approaching as near as they do to whole numbers. Taking from the table published by Richards the nine values given to three decimal places, he has calculated the chances against their approaching so near to whole numbers, using a formula given by Laplace. He finds that the probability is only about 1 in 1050, so that it may be considered practically certain that it is not purely by chance that so many of the numbers bear a comparatively simple ratio to the atomic weight of oxygen.

M. Rudolph (*Chem. Zeit.*, 1901, xxv., 1134) has similarly calculated out the probability figure for the eighteen atomic weights given to two places of decimals in the "didactic" table issued by the Germany Chemical Society, the values being referred to $H = 1$. It is thus found that the chances are 135 to 1 against the numbers falling out

as they do. I have calculated the probability also for the same eighteen elements using the standard $O = 16$, and I find that here the chances are 4120 to 1 against their approaching so closely to whole numbers. When these atomic weights are referred to $O = 16$ their tendency to approach whole numbers is therefore about thirty times as great as when they are referred to $H = 1$. In the case of an element whose atomic weight is not very high the difference between the two values is but small. The value found for the $H = 1$ table may therefore be due merely to the tendency of the atomic weights to approach whole numbers in the $O = 16$ table. To test this point I excluded the seven atomic weights below 30, and calculated the figure for the other eleven. The probability then rises as high as 1 to 4; that is to say, there is no tendency practically to approach whole numbers in the atomic weights above 30 when referred to $H = 1$. In the case of the $O = 16$ table the probability figure was still only 1 to 37, although all the atomic weights excluded are very near whole integers except that of magnesium.

There is, therefore, a distinct tendency for at least some of the atomic weights to approach whole numbers when $O = 16$. This may be due either to a general inclination of all the atomic weights, or the peculiarity may be confined to a few only, the others being governed by chance. Among the eighteen atomic weights ($O = 16$) there are three which are exactly integers as nearly as can be ascertained—carbon, phosphorus, and cobalt. To these may be added hydrogen (1.0075), the exact value of which is still not quite certain, and may be unity. When these four atomic weights are excluded, the remaining fourteen give a probability figure of 1 to 47. On the other hand, the probability of there being among eighteen numbers four which do not differ from complete integers by more than 0.0075 is only 1 to 7660. From these calculations it appears to be not impossible that the tendency to be whole numbers when $O = 16$ may be confined to quite a few elements.

Prout's hypothesis was definitely disproved by careful atomic weight determinations carried out by various workers, but especially by Stas. But as has been demonstrated, the tendency of certain atomic weights to approach whole numbers cannot be attributed entirely to chance. Although it has been universally the custom to refer all atomic weights either to $H = 1$ or $O = 16$, there is no fundamental reason why this should always be done. The atomic weights were first referred to hydrogen as unity, because that element had, and still has, the lowest atomic weight known. As the ratio between the atomic weight of hydrogen and those of the other elements cannot be determined with great accuracy, it is now more usual to refer the atomic weights to $O = 16$. For practical purposes it is essential that a standard be selected and rigidly adhered to, and the standard $O = 16$ is, on the whole, the most convenient. For the purpose of theory, however, there is no reason why other standards should not be adopted. The choice is large, as the atomic weight of any element may be given any value whatever, and the other atomic weights be then re-calculated from it.

Some three years ago the idea occurred to me to try whether some regularities might not be found between the values which Stas had determined with such accuracy. Taking first the atomic weights of chlorine and bromine, I found that the simplest numbers which expressed their ratio with a sufficient degree of accuracy are 90:203. Dividing these numbers by the factor 2.5387, the atomic weights found are 35.451 and 79.962, whereas the figures in the table of the German Committee are 35.45 and 79.96. There is nothing remarkable about this. It was only to be expected that the ratio could be expressed by means of five figures. I next used this factor to multiply the atomic weight of iodine, and I was agreeably surprised to find that it came out very near a whole number. What was still more remarkable was that the same thing occurred with silver. These results are shown in Table I.

* From the *Chemiker Zeitung*, July 19, 1902.

TABLE I.

Element.	Ratio.	Factor.	Atomic wt.	In table of German Com.
Cl ..	90	$\div 2.53868 =$	35.451	35.45
Br ..	203		79.963	79.96
Ag ..	274		107.930	107.93
I ..	322		126.838	126.85

These results can hardly be due to simple chance. I hesitate, however, to apply the theory of probabilities in this case, because I have myself selected the elements dealt with. Fluorine apparently does not fit into this scheme, nor does cyanogen. Several other elements, however, give figures approaching whole numbers when multiplied by the factor, but this is probably due entirely to chance.

The researches of Stas dealt not only with the above four elements, but also with the alkali metals. Mere inspection of the figures in this case shows that values very near can be obtained by multiplying whole numbers by the factor 1.004.

TABLE II.

Element	Ratio.	Factor.	Atomic wt.	In table of German Com.
Li ..	7	$\times 1.004 =$	7.028	7.03
NH ₄ ..	18		18.072	18.07
Na ..	23		23.092	23.05
K ..	39		39.156	39.15
Rb ..	85		85.34	85.4

Except in the case of sodium the values are identical, and even in that case the difference is not great. Other elements whose atomic weights give practically whole numbers when divided by 1.004 are:—Pb, Cd, V, Pt, Sn, Ca, Al. In practically none of these cases, however, are the atomic weights known with any great accuracy, and as most of the elements in question are distributed through the Periodic Table in apparently haphazard manner I prefer to ascribe these results to mere chance.

In spite of the enormous amount of time, skill, and ingenuity which have been devoted to the determination of the atomic weights, the degree of accuracy with which the majority of them are known is too small to allow of this investigation being carried very far. Nevertheless, a very remarkable regularity appears in the horizontal series of elements from vanadium to zinc inclusive, as is shown in Table III.

TABLE III.

Element.	Ratio.	Factor.	Atomic wt.	In table of German Com.
V ..	54	$\div 1.0551 =$	51.18	51.2
Cr ..	55		52.13	52.1
Mn ..	58		54.97	55.0
Fe ..	59		55.92	55.9
Ni ..	62		58.76	58.7
Co ..	—		—	59.00
Cu ..	67		63.50	63.6
Zn ..	69		65.40	65.4

Here, again, the agreement is absolute except in the case of copper, where the difference only amounts to 0.1. It may be mentioned that Ostwald gives the atomic weight of copper as 63.44. Cobalt does not fit in with the other elements at all, but the researches of T. W. Richards tend to show that the ratio O:Co = 16:59 exactly.

The facts here pointed out are remarkable, and so far as I know have not been observed before. There are evidently some unexplained regularities in the ratios of the atomic weights. As to the theoretical significance of these regularities, in the present state of our knowledge it appears somewhat premature to discuss it, but there is evidently a connection between the regularities and the phenomena of isomorphism.

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COMMON ERRORS IN THE DETERMINATION OF SILICA.*

By W. F. HILLEBRAND.

(Concluded from p. 81).

Causes of the Solubility of Silica under the Conditions Given.

In explaining the partial solubility of silica after drying at temperatures much above that of the water-bath it has been customary to assume the formation of soluble silicates by action between some of the silica and salts present. This is an undoubted cause, and one which should become more active with increasing temperature, though Gilbert's work does not seem to indicate this except when magnesium is present in quantity. But, if true at 120°, it must probably still be true to some extent at 100°.

Another explanation for the incomplete dehydration at 100° is assumed to be the protecting influence of other salts, and to remedy this, repeated additions of acid—or, perhaps better still, of water—are sometimes resorted to (see Experiments 10–12 of Table II.).

Again, it may be that the silica separated is itself soluble enough in acid to cause an appreciable error. The experiments reported below show clearly what the action of hydrochloric acid is on silica which had been obtained by fusing quartz with sodium carbonate and drying the evaporated hydrochloric solution for twenty-one hours on the steam-bath. This silica (about 0.65 gm.) was first extracted with a little acid, then thoroughly washed with hot water, rinsed back into the dish, and digested with hydrochloric acid of about 1.10 sp. gr. under varying conditions.

- Digested twenty-five minutes on the steam-bath with about 25 c.c. acid. Silica in filtrate 0.0029 gm.
- Same silica further treated as in a for one and one-half hours. Silica in filtrate 0.0026 gm.
- Same silica gently boiled in platinum for thirty minutes with above acid. Silica in filtrate 0.0022 gm.

There was thus extracted with ease nearly 1.2 per cent of the total silica without counting the probably larger amount held by the original filtrate, and it is to be presumed that the effect of the boiling would have been greater had it preceded instead of followed the quiet digestion.

It is thus plain how a portion of the silica always found in the filtrates gets there and that it is hopeless to try to prevent this by a single prolonged drying. Once the bulk of the silica is removed by filtration, however, then, after a second evaporation, because of its tendency to collect in clots of sensible size and consequent small surface exposure, the amount of silica going into solution is very small, and by no means in proportion to that of the acid used.

Determination of Silica that has Escaped Separation by the Usual Processes of Dehydration.

I pass now to another phase of the determination of silica, which, so far as I am aware, has never been investigated.

While it has long been known that some silica passed into the filtrate in silicate work, it was supposed to be recovered in the ordinary course of analysis with the ammonia or basic acetate precipitate, whence after ignition and weighing it could be obtained in insoluble form by fusing the mixture with potassium pyrosulphate. I purpose showing that these suppositions are both in part erroneous, that the residual silica is, as Lindo says, not wholly precipitated by ammonia, and that the ordinary treatment of

* Read at the Philadelphia Meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, vol. xxiv., No. 4.

the pyrosulphate fusion mass recovers but a minor part of that which was thrown down with the oxides of iron and aluminum.*

The experiments of Table IV. were made with a hydrochloric solution containing 0.0101 grm. of silica in 10 c.c. and with a solution of aluminum chloride free from silica. The amounts used were chosen to represent approximately the conditions most frequently prevailing in silicate analysis after but a single evaporation to separate silica. Precipitation was effected by ammonia at boiling temperature in a solution of about 300 to 400 c.c. volume containing 25 c.c. of hydrochloric acid of 1.10 sp. gr. As soon as settled, the alumina was filtered, washed, ignited, and fused with potassium pyrosulphate free from silica. The fused mass was generally dissolved in hot water acidulated with sulphuric acid, and once in warm water only, and the residual silica was collected, weighed, and corrected by hydrofluoric acid. In two cases (8 and 9) the filtrates were evaporated with excess of sulphuric acid, heated till fumes came off in quantity, and the separated silica collected after cooling and dilution of the solution. The filtrates from the alumina were evaporated, ignited to remove ammonium chloride, and the silica recovered by evaporation with a few drops of hydrochloric acid and further treatment as usual.

TABLE IV.—Silica in Alumina and in Filtrate from Alumina after One Precipitation by Ammonia.

	Al ₂ O ₃ used.	SiO ₂ used.	SiO ₂ in filtrate.	SiO ₂ recovered from Al ₂ O ₃ .	SiO ₂ recovered from K ₂ S ₂ O ₇ solution.
1.	0.19	none	none	none	—
2.	0.19	0.0101	—	0.003	—
3.	0.19	0.0101	—	0.0037	—
4.	0.19	0.0101	0.0020	—	—
5.	0.19	0.0101	0.0021	—	—
6.	0.19	0.0101	0.0007	0.0034	—
7.	0.19	0.0101	0.0019	0.0021	—
8.	0.20 (a)	0.0101	0.0007	0.0033	0.0060
9.	0.19	0.0101	0.0021	0.0023	0.0058

(a) Fe₂O₃.

Treatment of about 0.01 grm. of ignited precipitated silica with fused pyrosulphate resulted in the solution of 2 mgrms. of it and of 2.2 mgrms. in another test. Not being evenly distributed through a mass of other oxides undergoing solution, the solvent effect of the pyrosulphate in these cases may reasonably be supposed to be less than in the tests of the table.

We see here how in practically all ordinary silicate analyses a portion of the silica, sometimes very small, escapes being weighed at all, since it mostly passes on into the filtrate from the magnesia. When a double precipitation by ammonia or sodium acetate is made, instead of one as in the above tests, the loss will be greater than the table shows.

We further see how, when correction is made for the silica with the alumina, it is only in small part recovered and the alumina is consequently made to appear too high when determined indirectly. Here we have an added argument in favour of endeavouring to collect all silica at the outset, for it is shown that the expectation of recovering the whole of a missing portion later is based on erroneous assumptions. Therefore Gilbert's conclusion, because he found very little silica with the alumina after fusion with

pyrosulphate, that there is "no tendency for silica to recombine with the lime and alumina" (in non-magnesian silicates) "even at a temperature of 280° C." (*Technology Quarterly*, 1890, iii., 63), is perhaps not well founded. Since his further conclusion that silica is almost completely dehydrated at 120° (*loc. cit.*, p. 64) is based on this same reason, his analytical results lose much of their value.

As showing the errors in the silica results that may be incurred in the analysis of certain siliceous ores where potassium pyrosulphate is employed as the means for breaking them up, I will here give the figures for two titaniferous magnetites. The lower values give the silica obtained in the usual way from the mixture of silica and silicates left after fusion with pyrosulphate, and the higher those afforded by direct fusion of the ores with sodium carbonate.

	I.	II.
Silica	{ 11.73 12.42	{ 20.82 21.42

Complete analysis of the ores showed such a deficiency when pyrosulphate was used that the cause was sought, and found to be as stated above. It was this observation which led to a portion of the work summarised in Table IV.

The Proper Temperature for Ignition of Silica.

Most authorities, Fresenius included, have directed that blast temperatures be used in order to obtain the correct weight of ignited silica. It is only recently that doubt has arisen as to this because of the experiments of Lunge and Millberg (*Zeit. Angew. Chem.*, 1897, p. 425), who, employing silica derived from silicon tetrafluoride, observed no further loss in weight over the blast after sufficient exposure to the full flame of a good Bunsen lamp. This was in direct conflict with all my experience in silicate work, and as a result of friendly correspondence Professor Lunge caused the matter to be re-investigated in his laboratory a year ago, and sent me the following table of results, which I take the liberty of making public:—

TABLE V.—Loss in Weight of Pure Silica from SiF₄ at different Temperatures, as Determined by Dr. Lohöfer, in Professor Lunge's Laboratory.

Temperature.	Time. Minutes.	a.	b.	c.
105°	—	0.1840	0.1778	0.2020
Dark redness	30	0.1643	0.1584	0.1803
"	30	0.1640	0.1584	0.1800
Full flame of burner ..	30	0.1622	0.1566	0.1779
"	30	0.1620	0.1564	0.1778
Blast	30	0.1619	0.1564	0.1776

It is but natural that Professor Lunge should write:—"From these results I must conclude that Millberg and myself were right."

The following two tests by myself on silica similarly obtained confirm the above, and show, after blasting, further slight losses comparable with those appearing in Professor Lunge's table and of the same order as those produced by more than half-an-hour's blasting with silica precipitated by acid (see Table VIII.).

TABLE VI.—Showing Loss in Weight of Pure Silica from SiF₄, according to Tests made by Myself.

	a.
Full burner flame, thirty minutes	0.5053
Blast flame, thirty minutes	0.5017
	0.5014
	b.
Full burner flame, forty-five minutes	0.5030
Full flame, forty-five minutes	0.4997
Blast flame, forty minutes	0.4995
	0.4991 (a)

(a) This loss is partly chargeable to the crucible itself.

* Lindo (*CHEMICAL NEWS*, 1889, ix., 14) gives no quantitative data, and in all his experiments (with glass) the ammonia precipitates were, of course, very small. It is fair to conclude from his addition of ferric chloride to the filtrates from them in order to recover by its precipitation by ammonia the "last trace" (*loc. cit.*, p. 40) of silica, that he would not have suspected the presence of any silica in these filtrates when analysing mixtures containing considerable aluminum or iron oxide. Lindo's observations are of value, but his analytical results are not, for the reason that he operated largely in glass vessels and his alkaline solutions remained long in contact with glass, hence must have taken silica from them, notwithstanding which his analyses show without exception a large loss.

These slight losses are not due to mechanical carrying off of silica, for the latter had utterly lost its extraordinarily down like character during the early heating and become converted by the blasting into a coherent cake of enormously reduced bulk.

Let me now, however, present another series of results furnished by silica otherwise precipitated. The silica used was obtained by three evaporations from the quartz that served for the earlier experiments of this paper, and the initial weights are those found after an exposure of about one hour to the full Bunsen flame. The weights given represent the silica as corrected by hydrofluoric and sulphuric acids for the few tenths of a milligram of non-volatile salts always present. The crucibles were found not to lose weight themselves over the blast. The quartz powder employed was 99.88 per cent pure, as found by careful evaporation with hydrofluoric and sulphuric acids.

TABLE VII.—Showing Differences in Weights of Silica Precipitated from Sodium Silicate when Ignited over Bunsen Burner and Blast-lamp.

	Weight of quartz.	Silica found.		Loss in weight.	Percentages found.	
		Burner, one hour.	Blast, half hour.		Burner.	Blast.
1.	0.5738	0.5761	0.5735	0.0026	100.40	99.95
2.	0.5931	0.5945	0.5930	0.0015	100.24	99.98
3.	0.6401	0.6450	0.6394	0.0056	100.76	99.90
4.	0.6638	0.6668	0.6628	0.0040	100.45	99.85
5.	0.7028	0.7058 (a)	—	—	100.25	—
6.	0.7309	0.7342	0.7306	0.0036	100.45	99.96
7.	0.8208	0.8271	0.8206	0.0065	100.77	99.98
8.	0.8495	0.8521	0.8484	0.0037	100.31	99.88
9.	0.8943	0.8996	0.8936	0.0060	100.59	99.92
10.	—	0.9989	0.9898	0.0091	—	—

(a) Two hours.

Results similar to the above are repeated in every silicate analysis that is made in our laboratory, and others have told me their experience is the same. It is as clear as daylight that the blast is a necessity if the work is to be at all accurate. In every one of the above instances the percentage found without blast is far in excess of 99.88—the true value for silica in the quartz,—and is as invariably brought very near this value, and with far smaller variations from a mean, when the blast is applied (see below). The above values for “burner” percentages very well represent the usual lack of exact agreement in series of duplicate silica determinations when the blast has not been used (see Gilbert's paper), while those of the next column show of what accuracy the determination is susceptible when all the conditions of success are understood and applied.

From the foregoing it appears that the silica separated by water from silicon tetrafluoride, and that by hydrochloric acid from sodium silicate, are in different conditions and behave differently when strongly heated; that Professor Lunge's conclusion that silica need not be blasted, while correct for one form of silica, cannot be applied, as he supposed, in analytical work.

I have always, until lately, regarded one-half hour's blasting as sufficient in all cases for as much as a grm. of silica, but that this length of time is often insufficient to secure constant weight is indicated by some of the results in Tables V. and VI., and still more by those in Table VIII.

TABLE VIII.—Showing Need of very long Blasting at Times.

Heat.	Time in minutes.	Weights of silica.					
		1.	2.	3.	4.	5.	6.
Burner	60	0.6691	0.7041	0.9989	—	0.4175	0.4220
Blast	30	0.6657	0.6982	0.9905	0.7208	0.4154	0.4192
„	30	0.6656	0.6979	0.9902	0.7201	—	0.4187
„	30	0.6651	—	0.9899	0.7193	0.4152	0.4185
„	30	—	—	0.9897	0.7194	—	—
„	30	—	—	—	0.7194	—	—

The progressive losses shown here are not chargeable to the crucibles, nor were they due to mechanical loss of silica or to volatilisation of included salts, and they explain very well the fact that nearly all the figures of the first column in Table V. slightly exceed the true value for silica in the quantity used, for they were obtained by blasting for only one-half hour. They may also serve to explain in small part the excessive summations often encountered in rock analyses. These later losses can exert little effect when the silica percentages are small, but when large, as in rock analysis, they may at times be of moment and necessitate blasting for more than half-an-hour.

In the foregoing I have entered into such detail as the exact scientific worker needs for his enlightenment, and have carried my separations and ignitions farther than the technical chemist ordinarily cares to or can proceed. But in its main features, what I have said concerns him not less than the research chemist, and I trust that in some respects it may help to ease his path.

Summary.

Statements of earlier writers are fully confirmed, that silica cannot be rendered wholly insoluble by a single or any number of evaporations with hydrochloric acid when followed by a single filtration, no matter what temperature may be employed, but that two or more evaporations alternating with filtrations are necessary to secure satisfactory results.

It is shown that the generally accepted view that any silica passing into the filtrate is wholly thrown down by ammonia or sodium acetate in presence of much aluminum or iron is incorrect. Also that silica is appreciably soluble in melted potassium pyrosulphate, and that, consequently, when siliceous oxides of iron and aluminum obtained in analysis are then fused, their silica contents are only in small part left undissolved when the fused mass is taken up with water or acid. Both these sources of error are avoided by separating all silica at the start as above.

The need of blast ignition in order to get the correct weight of silica obtained in analysis is proved. The opposite conclusion of Lunge and Millberg, being based on what seems to be a different behaviour of the silica derived from silicon tetrafluoride, is therefore not justified.

THE POSSIBLE SIGNIFICANCE OF CHANGING ATOMIC VOLUME.*

By THEODORE WILLIAM RICHARDS.

(Concluded from p. 83).

HAVING thus plausible inference, from independent sources, as to the relative values of the compressing agencies existing in metals at the ordinary temperature, it is worth while to study the correction which must be applied to the volume change exhibited in chemical combination with another element. In zinc the self-affinity is so great (boiling-point = 1200° A), and the metal is hence already so compressed, that a given further pressure causes less change in its volume than it would cause in the case of mercury. That is, the mercury contracts more than zinc when it is oxidised. Hence the difference between the volume of the oxide and the volume of the metal gives too low a value for the volume of the combined oxygen in the case of mercury. Thus the contraction of the oxygen is really less in the case of mercuric oxide, although it appears to be the same.

Without going further, one can explain by means of these considerations the behaviour of zincic and mercuric oxides, when subjected to high temperatures. The 16 grms. of oxygen in mercuric oxide occupies a larger space than an equal weight in the case of zinc, hence one infers

* From the *Proceedings of the American Academy of Arts and Sciences*, xxxvii., No. 1.

that it is less compressed by its affinity, hence the affinity must be less. This smaller affinity should be more easily overcome by rising temperature, a prediction which agrees with facts. Thus there appears to be in this case a connection between the compression of substances and their tendency to combine one with another.

The case under consideration is typical. In the case of sodium and magnesium, the affinity of the metal for oxygen is so enormous as to overcome easily the large affinity of the metal for itself, and besides this to compress both metal and oxygen together into a space smaller than that previously occupied by the metal. This fact corresponds with the great difficulty of decomposing sodic and magnesian oxides. Metallic magnesium probably has an energy-quotient a stress more than four times as great as sodium (see table on p. 83); hence the total contraction on combination with oxygen is less than in the case of sodium. Comparison with the cases of mercury and zinc will show that this small contraction does not necessarily conflict with the fact that magnesium decomposes sodic oxide at high temperatures. Again, the contraction involved in the formation of argentic oxide is very slight. In this case the large volume of oxygen is not concealed by the contraction of the metallic element, as it was in the case of mercury, for silver is not particularly compressible. Hence one can infer that the affinity of silver for oxygen is smaller than that of magnesium for oxygen—an inference which agrees with fact. Moreover, since the relation is nearly additive, that is, neither silver nor oxygen change much in volume on combination, their combination is easily shifted; that is to say, silver oxide is easily decomposed by heat.

Of course many tables comparing the molecular volumes of solids and liquids might be drawn up, since a very great number of specific gravities have been determined. A table containing chlorides of the metals already considered may be of interest.

Molecular Volumes of Chlorides

Sub- stance.	Weight of metal combined with 35.5 grms. chlorine.	Density of metal.	Density of chloride.	Volume of given weight of metal.	Volume of corre- sponding chloride.	Excess of volume of chloride above metal.
Ag ..	108	10.56	5.53	10.27	45.90	+15.63
$\frac{1}{2}$ Hg ..	100	14.00	5.42	7.30	25.5	+18.2
Hg ..	200	14.00	7.10	14.00	33.2	+19.2
$\frac{1}{2}$ Cu ..	31.8	8.95	3.05	7.10	25.4	+18.3
$\frac{1}{2}$ Co ..	28.5	9.00	2.94	3.16	21.8	+18.64
$\frac{1}{2}$ Cd ..	56.2	8.67	3.7	6.47	24.8	+18.33
$\frac{1}{2}$ Zn ..	32.7	6.9	2.753	4.75	25.0	+20.25
Mg ..	12.2	1.74	2.177	7.0	21.95	+15.00
Na ..	23.05	0.973	2.15	23.7	27.2	+4.2
K ..	39.14	0.875	1.995	45.7	37.3	-8.4
Rb ..	85.44	1.52	2.21	56.1	55.0	-1.0
H ..	1.01	0.07	1.27	14.1 (?)	28.9	+14.7

Combined with carbon 22.8

Liquid chlorine at -80° (boiling-point, 760 m.m.;

sp. gr. = 1.66) 21.5

Liquid chlorine at $+80^{\circ}$ (sp. gr. = 1.20) 29.6

Here the variations in contraction are less than they were before. Chlorine evidently possesses more equally distributed affinities than oxygen does, and apparently somewhat weaker ones. The two most interesting features of this table, which may be seen without the elimination of the self-affinities of the several metals, are the small excess in the case of silver, and the larger excess in the case of mercurous chloride. This is quite in accord with the facts; for argentic chloride is more stable than the oxide, and mercurous chloride easily splits into mercuric chloride and mercury (Richards, *Proc. Amer. Acad. Arts Sci.*, 1897, xxxiii., 9).

The case of the hydroxides is especially interesting.

Molecular Volumes of Hydroxides.

Sub- stance.	Weight of metal combined with 17 grms. hydroxyl.	Density of metal.	Density of hydroxide.	Volume of given weight of metal.	Volume of corre- sponding hydroxide.	Excess of volume of hydroxide above metal.
Ag ..	The hydroxide is exceedingly unstable.					
$\frac{1}{2}$ Hg ..	It is doubtful if the hydroxide exists.					
$\frac{1}{2}$ Cu ..	The hydroxide cannot be dried without decomposition.					
$\frac{1}{2}$ Co ..	28.5	9	3.597	3.16	12.67	+9.51
$\frac{1}{2}$ Cd ..	56.2	—	4.79	6.47	15.25	+8.78
$\frac{1}{2}$ Mg ..	12.2	—	2.36	7.0	12.90	+5.90
$\frac{1}{2}$ Sr ..	43.83	2.54	3.62	17.3	17.0	-0.3
Na ..	23.05	0.973	2.13	23.7	18.80	-4.9
K ..	39.14	0.875	2.044	45.7	27.5	-18.2

Hydroxyl in organic compounds +12.0

Hydroxyl in hydrogen dioxide (sp. gr. = 1.50) 11.4

The density of the hydroxide of zinc has not been accurately determined; indeed, the data concerning cobalt, cadmium, and magnesium are not very trustworthy on account of the amorphous condition of most hydroxides. It is interesting to note that in this table, where the substances are arranged in the order of the contraction which ensues when hydroxyl combines with the metal, should also be arranged in the *electrochemical order*. That is to say, the solution tension of a metal appears to be associated with the excess of affinity of the metal for hydroxyl over its affinity for itself, and intensity of potential seems to be associated with intensity of atomic compression. The inference to be drawn from this comparison is, of course, that the formation of the metallic ion in water is connected with the affinity of the metal for water—an affinity which manifests itself even when both of the "bonds" of oxygen are filled.* Similar attraction for nitrogen or sulphur would explain cases in which the solvent does not contain oxygen.

If this is true, contraction should take place when salts are dissolved in water. This inference is amply verified by facts. In some cases the solution occupies even less space than the water alone, involving a total contraction greater than the volume of the salt itself. The best known of these cases are those of lithic, sodic, and baric hydroxides, and cobalt, nickel, zinc, and magnesium sulphates, but undoubtedly others exist (Thomsen, "Thermochimische Untersuchungen," 1882, I., 45; MacGregor, *Trans. Roy. Soc. Canada*, 1890, p. 19; 1891, p. 15; *Trans. Nova Scotia Inst. Nat. Sci.*, 1890, vii., 368). In a large majority of cases when an electrolyte is dissolved in water, the sum of the volumes of salt and of the solvent taken together considerably exceeds the volume of the solution. This contraction is usually ascribed wholly to the dissolved substance in dilute solutions (Van't Hoff, "Vorlesung, Phys. Theoret. Chem.," 1900, III., p. 41; Drude and Nernst, *Zeit. Phys. Chem.*, 1896, xv., 79, ascribe this contraction to "electrostriction"), but it seems to me that the behaviour of the salts named above proves the falsity of this method of calculation. *The water as well as the salt must contract when a salt is dissolved.* So many complications are concerned in the act of the solution of an electrolyte that it is difficult to unravel the tangled clues; but the wide deviations exhibited by different substances seem to indicate that there are present overlapping contractions and expansions, the resultant of which is a smaller quantity than some of the individual influences. Such contractions and expansions are just what one would expect to find in a readjustment of affinities.

In considering the simpler case of solid non-electrolytes, one usually finds here also a contraction upon solution, although less marked than in the extreme cases named above. For this reason, one is inclined to ascribe the act of solution of all kinds primarily to the affinity of the

* Brühl has suggested that oxygen is the cause of dissociation, but he ascribes it rather to quadrivalence than to a general affinity.

solvent for the dissolved substance. The solution tension of a metal or salt becomes simply a balance or ratio of attractions—the separating tendency of heat upon the dissolving phase is much assisted by the attraction from outside. This is of course no new idea. The possible method of treating mathematically these balanced influences is suggested in a recent paper on the “driving tendency” of reaction (Richards, *Journ. Phys. Chem.*, 1900, iv., 385; see specially p. 391).

That electrolytic separation also should be assisted by the outside attraction for the solvent is almost a foregone conclusion. This may be inferred from the contraction shown by most electrolytes on dissolving. Hence may arise the various contact-potentials exhibited by the same substance in different solvents; for different solvents must possess different affinities. Hence also one would expect to find a much greater potential needed for the dissociation of gases than for that of dissolved substances.

The mechanism of electrolytic dissociation in gases is now usually explained by the aid of the ingenious hypothesis of “electrons,” as amplified by J. J. Thomson and his students in the brilliant experimental researches published in the recent volumes of the *Philosophical Magazine*. This daring hypothesis must not be accepted without reservation, however. Some physical objections to it have been suggested by Ernest Merritt in his interesting address to the American Association for the Advancement of Science (*Proc. Amer. Assoc. Adv. Sci.*, 1900, p. 49); and other objections arise when one tries with its aid to unravel the tangle of influences involved in purely chemical action. The rejected alternative of imagining the atom as indivisible, but as capable of receiving widely varying electric charges under widely different conditions, has some advantages which the opposite hypothesis does not possess. The subject is much too large for discussion here, however. One phase of it, which bears directly upon the subject of the present paper, may receive brief notice.

The results of Thomson, Townsend, Zeleny (*Phil. Mag.*, 1898, [5], xlv., 120; see also *Amer. Chem. Journ.*, 1901, xxv., 340, for a *résumé* of this work), and others seem to indicate that the bearer of the negative electricity not only carries the high charge referred to above, but that it is very small, while the bearer of the positive electricity is very large. May it not be the atom itself which thus expands and contracts? This agrees with the verdict of the results of atomic compression given above. Change of atomic volume seems to be associated with electric stress. This assignment of electric expansibility to the atomic sphere of influence might explain other phenomena concerning the behaviour of electrified gases; for example, the increase of pressure which is observed when a gas is highly charged (De la Rue and Müller, *Phil. Trans.*, 1880, 86). Again, the great conductivity of a gas with adequate potential and quantity of electrical discharge seems to indicate that then the situation must resemble that in a metal, where the spheres of stress fill the whole volume occupied by the substance (Trowbridge and Richards, *Phil. Mag.*, 1897, [5], xliii., 349). The temperature must be so high under these circumstances that the gas is probably in a condition of thermal dissociation. Hence one is inclined to refer the great conductivity to the electrical susceptibility of evenly compressed or undistorted atoms. The fact that pure metals conduct electricity better than alloys or compounds seems to support this conclusion. The permeability of solids to cathode rays might be explained by supposing that the smallest particles of both solid and gas are much contracted by the negative charge.

It is with some diffidence that this paper attempts to reconcile the facts with any hypothesis, for hypotheses sometimes lead to dangerous delusions. If, however, one never forgets the essential difference between fact and hypothetical inference, a theory may afford useful suggestions for further research. The facts under discussion in the present paper seem to me to be adequately connected by none of the current conceptions concerning

atoms, hence it has seemed not wholly pointless to postulate a theory which might serve better. The essential elements of this theory must be evident from the trend of the hypothetical discussion above; they are not wholly new. Since changes of atomic volume seem to be so closely associated with the most intimate properties of substance, it seems necessary to assign more importance to the atomic “sphere of influence” or the “free space” around the atomic centres than is customary. Indeed, the properties of material seem to be as much concerned with the “atomic shell” as with the “atomic centre.” The two hypothetical conceptions are so closely related as to be inseparable.

Such a point of view leads to the conception of an atom as a compressible field of force possessing two attractive attributes, chemical affinity and gravitation, both of which may be concerned in chemical action. Mass may be supposed to be casually connected with gravitation. The fact that in many cases affinity diminishes with increasing atomic weight,* taken together with the Laws of Faraday and of Dulong and Petit, suggests that the two attractive forces in the atom may bear some sort of reciprocal or additive relationship to one another—that the product or sum of the two may afford a constant basis for the vibrations of heat and electricity. This relation is often hidden by electrical attraction, which plays so important a rôle in chemical action that it is sometimes hard to distinguish the intensity of chemical affinity proper. In such an atom one can imagine that either thermal or electrical vibration might cause distention. The phenomena of electricity suggest that electricity plays around the atomic surface, while heat seems to be concerned with a more fundamental or central agitation. Light-vibration, which seems also to be intimately concerned with atomic structure, would be assumed to be a surface effect like electrical vibration.

Such an atom would be compressible under the influence of its own affinities as well as under the influence of external pressure. Permanent atomic distortion would accompany chemical union, and the heat of the reaction would be the outcome of the resulting decrease of internal energy. Atomic volume and atomic compressibility might limit the possibility of distortion; hence would arise a possible explanation for quantivalence, stereochemistry, and crystal form. Many other properties of materials, too numerous to mention, seem to be explicable in a similar way.

It would be unreasonable to expect the hypothesis thus briefly described to correspond to all known facts. No hypothesis has ever been proposed which is wholly satisfactory; our knowledge is incommensurate with the possibilities involved. If, however, a given theory is found to explain some relationships better than other hypotheses, it may be of service in suggesting new experimental research. Such a service is of course the best one which a hypothesis can perform.

The idea discussed above has been already applied in plausible fashion to a wide range of chemical and physical phenomena. If future experimentation to be carried on here seems to warrant it, these applications may form the subject of another communication.

The object of the present paper may be summed up in a few words, as follows:—It is pointed out that changing atomic volume may be used as an approximate measure of the pressure which causes it, and therefore of the affinity which causes the pressure. Some of the difficulties in the way of exact interpretation are pointed out, and hints are given as to possible modes of overcoming the difficulties.

The chief outcome of the paper is the following postulate:—*The atomic volume is not constant, but a function of pressure and temperature, and probably of electric stress.*

* Van't Hoff, *Vol. Th. Phys. Chem.*, III., 1900, 87. Compare also the relation of the energy-quotients of similar metals referred to in the present paper (p. 83).

In this connexion it is pointed out that chemical affinity is possibly a reciprocal function of mass.

To explain these and many other facts, a modification of the atomic hypothesis is tentatively proposed which contends that we have no right to disregard the compressible environments around the centres of gravity and affinity.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolitan Water Act, 1871.

London, August 11th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 216 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 216 samples examined by us chemically during the month, all were found to be clear, bright, and well filtered.

The prolonged drought still continues; the actual rainfall at Oxford during July was 0.62 inch, the average fall is 2.49 inches; this leaves a deficit of 1.87 inches, which, added to the previous one of 3.30 inches, gives a total deficit of 5.17 inches, or 38.8 per cent on the thirty-five years' average.

Our bacteriological examinations of 562 samples have given the results recorded in the following table; we have also examined 40 other samples, from special standpipes, wells, &c., making a total of 602 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 27 samples) ..	292
New River, filtered (mean of 140 samples) ..	7
Thames, unfiltered (mean of 27 samples) ..	2172
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 304 samples)	14
Ditto ditto highest	212
Ditto ditto lowest	0
River Lea, unfiltered (mean of 27 samples) ..	250
River Lea, from the East London Company's clear-water wells (mean of 37 samples) ..	44

Of the 481 samples taken daily from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, forty samples, or 9.7 per cent, were sterile. Only three samples contained more than 150 microbes, while but twelve samples, or 2.4 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the twelve excess samples was 149, against a corresponding mean of 206 in twenty-five samples during June.

The above results show that the water supplied to London during July was of exceptional purity, having regard to the average good quality of the London supply. It will be seen that the number of microbes is remarkably small, no less than 40 of the samples examined bacteriologically being sterile. But it must be remembered that the season is quite abnormal as regards rainfall, so that the Thames is delivering, practically, a considerable proportion of spring water.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

NOTICES OF BOOKS.

Essays on Historical Chemistry. By T. E. THORPE, C.B., LL.D., F.R.S., Principal of the Government Laboratory, London. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1902. Pp. 582.

THE present volume consists principally of lectures and addresses given at different times by the author during the last twenty-five years; these essays are now put together with the object of showing how the labours of some of the greatest masters of chemical science have contributed to its development. The book is mainly biographical, and includes short sketches of the lives of such men as Priestly, Cavendish, Lavoisier, Faraday, Dumas, Victor Meyer, Mendeleeff, and others.

"The Rise and Development of Synthetical Chemistry," which forms the subject of No. XVI. of this series, is of considerable interest; it first saw light as the Presidential Address to the Sutton Coldfield Institute in the year 1892, and traces the advance of synthetical chemistry from the first inception of the atomic hypothesis down to the triumphs of recent years, as illustrated by the artificial formation of indigo and that of the sugars, *dextrose* and *levulose*. The advance in every section of chemistry during the nineteenth century, and especially during the latter half of it, has been literally by leaps and bounds, and no branch has been more fruitful in results or possibilities than that of organic synthesis.

No. XVII., on "The Progress of Chemistry in Great Britain and Ireland during the Nineteenth Century," covers the ground from the beginning of the last century to the foundation of the Chemical Society in 1841; and No. XVIII., on "The Development of the Chemical Arts during the Reign of Queen Victoria," brings us up to comparatively recent times.

The book is well worth looking through, and contains a large amount of interesting matter.

Higher Mathematics for Students of Physics and Chemistry. By J. W. MELLOR, D.Sc. London: Longmans, Green, and Co. 1902.

THIS book is intended for those who require a practical knowledge of higher mathematics to enable them to deal with, and interpret from a mathematical point of view, the results of physical and chemical experiments. The reader is supposed to possess only a very elementary knowledge of algebra and trigonometry, and even this minimum is recapitulated for the benefit of those who have forgotten their school-work. The book is divided into three parts. Part I. (Elementary) deals with the Differential Calculus, Analytical Geometry, and the Integral Calculus. As far as possible, all examples are based upon figures obtained in actual experiments or well-known formulæ, and thus no opportunity is lost of incidentally adding to chemical knowledge. As is to be expected, the discussion of the integral calculus leads to most interesting pages on such branches of the subject as

chemical equilibrium, fractional precipitation, &c. The second part is occupied with advanced mathematics, and opens with a chapter on hyperbolic functions, and thence passes to the consideration of differential equations; this part will undoubtedly be found most useful, for the subject is treated quite fully enough for the purpose in view, and the student is saved from the necessity of making generally fruitless attempts to grapple with such difficult, though admirable, text-books as Forsyth's on the subject. The third part contains short expositions of the theories of equations, determinants, probability, and errors; this last forming one of the best and most interesting chapters in the book. A collection of useful results and formulæ is appended. The least mathematical of science students cannot help finding this volume attractive and useful; it may safely be said to have thoroughly fulfilled its aim, and will no doubt soon be regarded as indispensable to the student and teacher alike. The style in which it is written is very far removed from that generally associated with a mathematical text-book, and the freedom and graphic directness of some of the writing will do much towards investing the subject with a new interest.

Berichte über Land- und Forstwirtschaft in Deutsch-Ostafrika ("Reports on Agriculture and Forestry in German East Africa"). Band I. Hefte 1 und 2. Herausgegeben vom Kaiserlichen Gouvernement von Deutsch-Ostafrika. Heidelberg: Carl Winter's Universitätsbuchhandlung. 1902.

THESE Government reports of the Colonial department of the Foreign Office deal with questions relating to agriculture, and contain also discussions and articles on such subjects as the diseases of animals and plants, meteorological conditions, geography, and geology. The first number consists of extracts from the annual report for the year July 1, 1900, to June 30, 1901, of the district and military stations in various regions of German East Africa. These are chiefly concerned with agricultural activity, the export and import trades, and the results of the experimental cultivation of various foreign plants and trees. The second number contains articles mainly of biological interest, with the exception of the reports of chemical researches on some soils in the neighbourhood of Tanga in Usambara. Numerous analyses of the soil at various depths were made, and the results are tabulated here. With a few exceptions these results point to the fact that the soil of this region of German East Africa is singularly good.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by FRANZ HOFMEISTER. Band II. 7-9 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1902.

THIS number contains papers of much chemical interest. Amongst them may be specially mentioned Dr. B. Slowtsoff's report of his investigations of the action of the liver cells on copper, a continuation of his previously described researches on similar actions on arsenic and mercury. He establishes the fact that, like arsenic, copper, when administered in the form of sulphate, forms a compound with the nuclein of the liver; this compound, however, is attacked by 0.3 per cent hydrochloric acid, and destroyed by pepsin hydrochloric acid, and thus is not so stable as the arsenic compound. A paper by F. Simuely on melanins derived from albumen represents an immense amount of apparently most thorough and careful experimental work. The chemical behaviour of the artificial melanins has been subjected to an ably conducted inquiry, and the paper contains much useful information. Another article by R. Schröder on the protein substances of yeast is full of interest, though some of the author's results call for further investigation on the same lines.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

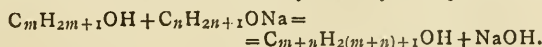
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 3, July 21, 1902.

Action of Hydrochloric Acid on the Sulphates of Aluminium, Chromium, and Iron Sesquioxides.—A. Recoura.—The author's experiments on the behaviour of solutions of the salts of sesquioxides of aluminium, chromium, and iron, when they are reacted upon by an acid different from that of the salt. He finds that the sulphate of chromium sesquioxide, for example, under the action of heat, dissolves a portion of the sulphuric acid set free. The result of this decomposition in presence of another acid weaker than sulphuric acid, such as hydrochloric acid, when used in great excess, has the power of fixing one or more molecules of hydrochloric acid, giving rise to a polyacid salt in which the hydroxyls of the base are saturated, some by the sulphuric, others by the hydrochloric acid. By using this method the author obtained the two polyacid salts, $\text{AlSO}_4\text{Cl}_6\text{H}_2\text{O}$ and $\text{CrSO}_4\text{Cl}_6\text{H}_2\text{O}$, whilst with the sulphate of iron he transformed ferric sulphate, Fe_2SO_4 , into an acid sulphate, $\text{Fe}_2\text{SO}_4\text{SO}_4\text{H}_2\text{H}_2\text{O}$.

Precipitation of Cupric Chloride and Bromide with Sulphuric Acid.—Georges Viard.—An excess of concentrated sulphuric acid gives a yellowish-brown precipitate of the anhydrous chloride when added to a solution of cupric chloride, and a black precipitate of the anhydrous bromide when added to cupric bromide. The same precipitates are produced by adding an excess of sulphuric acid to any cupric salt in presence of an alkaline chloride or bromide. This property gives a convenient distinction between chlorides and bromides, the best application being to prepare beforehand a mixture of 1 volume of copper sulphate with 10 volumes of H_2SO_4 . By adding to this reagent a few drops of the salt to be examined a yellow precipitate is formed if a chloride is present, a black precipitate if it is a bromide. Very dilute solutions may thus easily be recognised.

Cerium Silicide.—M. Sterba.—The author obtains a cerium silicide of formula CeSi_2 , different from M. Ulk's silicide. Its relative stability allows of its preparation in Moissan's electric furnace. Its properties are different from those of calcium silicide. It seems to approach the silicides of the heavy metals in properties.

Action of Alcohols on the Sodium Derivatives of other Alcohols.—Marcel Guerbet.—As a result of a previous research the author predicts the condensation occurring between certain alcohols and the sodium derivatives of other alcohols, e.g., between ethylic or propylic alcohols, and the sodium derivative of α -naphthyl alcohol. The reaction can be expressed by the equation:—

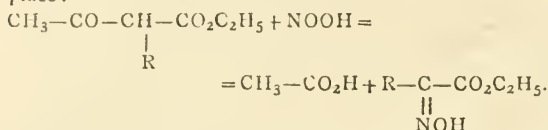


Investigation on the Simultaneous Distillation of two Non-miscible Substances.—Eug. Charabut and J. Rocherolles.—The two laws which the authors establish during the present research are contained in the following statement:—The proportion between the weight of a body non-miscible with water and the weight of water which simultaneously distils, varies in such a manner as to approach unity when the temperature increases without attaining the critical temperature of one of the two substances.

A New Iodinated Phenol.—P. Brenans.—The author prepares a new isomer of di-iodated phenol, $\text{OH}-\text{C}_6\text{H}_3\text{I}_2$ 1,3,6, from orthonitraniline. By mixing solutions of iodine chloride and orthonitraniline in acetic acid he prepares mono iodated orthonitraniline,

$C_6H_3(NH_2)(NO_2)(I)1.2.4$. The diazoic derivative of this last body can be decomposed by means of potassium iodide, and gives a di-iodated nitrobenzene, $C_6H_3(NO_2)(I)_21.3.6$. The corresponding base, di-iodated aniline, $C_6H_3(NH_2)(I)_21.3.6$, gives by diazotation and decomposition of the diazoic radical in presence of water, di-iodophenol, $OH-C_6H_3I_21.3.6$.

Action of Nitrous Acid in Acid Solution on the β -Ketonic- α -substituted Ethers. Synthesis of the Homologues of Pyruvic Acid.—L. Bouveault and R. Locquin.—The authors cause nitrous acid, not in alkaline solution, as previous experimenters have done, but in acid solution, to react on the α -substituted acetylacetic ethers, and they have established the fact that under these conditions it is always the following reaction which takes place:—



The reactions are perfectly definite. Nitrosation in acid solution of the β -ketonic- α -substituted ethers by any radical whatever, primary or secondary, yields exclusively, by separation of the acid radical, the oximes of substituted glyoxylic ethers. From this a very convenient method of preparing a great number of ethers of the homologues superior to the pyruvates can be deduced.

NORTHERN POLYTECHNIC INSTITUTE, HOLLOWAY, LONDON, N.

The Governors of the above Institute invite applications for the Post of HEAD of CHEMICAL DEPARTMENT. Salary £250 per annum for whole time service. Duties to commence on Sept. 18th, or as soon after as possible. Applications to be sent in by Sept. 3rd on special forms to be obtained from—

W. M. MACBETH, Clerk to Gov. R.O.S.
August 12, 1902.

THE SOUTH-WESTERN POLYTECHNIC, CHELSEA, S.W.

The Governing Body invite applications for the DEMONSTRATORSHIPS of CHEMISTRY and PHYSICS and the LECTURESHIP of MATHEMATICS. The remuneration attached to each of the three posts is £150 per annum. Candidates must apply on or before Sept. 2nd. Particulars of duties and forms of application may be obtained from the SECRETARY.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. (Incorporated by Royal Charter).

NOTICE IS HEREBY GIVEN, that a FINAL EXAMINATION in the Branch of BIOLOGICAL CHEMISTRY will be held at the Laboratories of the Institute on TUESDAY, OCTOBER 21st, 1902, and three following days.

The Syllabus of the Examination will include the following:—Biological Chemistry, with special reference to the Chemistry and Bacteriology of Foods, Water Sewage and Effluents, and the practical applications of Biological Chemistry to industries.

Candidates who have complied with the Regulations, and desire to present themselves for this Examination, are required to communicate with the Registrar before Tuesday, September 23rd next, when the List of Candidates for this Examination will be closed.

By Order of the Council,
RICHARD B. PILCHER, Registrar.
30, Bloomsbury Square, London, W.C., August 11, 1902.

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Complete Courses of Instruction are provided for Students of both sexes proceeding to Degrees in Science, or in Letters, and for Teachers' Certificates for Secondary Schools, and for the Diploma in Theory and Practice of Teaching. Special facilities are offered for the study of Agriculture, Applied Chemistry, Mining, and all branches of Engineering and Naval Architecture. Matriculation and Exhibitions Examinations begin September 29th. Lectures begin October 7th, 1902. Prospectuses on application to the Secretary.

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MATHEMATICS	E. H. SMART, M.A.
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ZOOLOGY	H. W. UNTHANK, B.A., B.Sc.
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The SESSION commences on OCTOBER 7th.

S. CHAFFERS, Registrar.

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THE REGISTRAR.

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The MATRICULATION EXAMINATION of SESSION 1902-1903 commences on OCTOBER 24. Matriculation Certificates of any University within the United Kingdom are accepted.

All Lectures, Scholarships, Exhibitions, and Prizes are Open to Students of either sex.

The Scholarship Examinations in Arts, Medicine, and Engineering commence on OCTOBER 23.

DEPARTMENTS OF

SCIENCE, MEDICINE, & ENGINEERING.

Mathematics	Prof. THOMAS J. T. BROWWICH, M.A., Fellow of St. John's College, Cambridge; Examiner, R.U.I.
Physics	Prof. A. ANDERSON, M.A., late Fellow of Sidney Sussex College, Cambridge; President of the College.
Chemistry	Prof. ALFRED SENIER, Ph.D., Berlin
Natural History, Mineralogy, and Geology	Prof. RICHARD J. ANDERSON, M.A., M.D., M.R.C.S., Eng.; Examiner, R.U.I.
Engineering	Prof. EDWARD TOWNSEND, M.A., D.Sc.; Examiner, R.U.I.
Anatomy and Physiology	Prof. JOSEPH P. PYE, M.D., M.Ch., D.Sc., F.R.U.I.
Practice of Medicine	Prof. JOHN ISAAC LYNHAM, M.D., M.Ch., M.A.O., F.R.U.I.
Surgery	Prof. W. W. BRERETON, L.R.C.S.I., M.R.C.P.I.
Materia Medica	Prof. NICHOLAS W. COLOHAN, M.D., M.Ch.
Gynaecology	Prof. RICHARD J. KINKEAD, B.A., M.D., L.R.C.S.I.

Prospectus of the Courses and Regulations for Scholarships, &c., can be had on application to the—

REGISTRAR,
Queen's College, Galway.

THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2231.

RADIO-ACTIVITY OF THORIUM COMPOUNDS.*

II. THE CAUSE AND NATURE OF RADIO-ACTIVITY.

By E. RUTHERFORD, M.A., D.Sc.,
Macdonald Professor of Physics, McGill University, Montreal,

and
FREDERICK SODDY, B.A. (Oxon.),
Demonstrator in Chemistry, McGill University, Montreal.

(Continued from vol. lxxxv., p. 308).

At the close of the first paper on this subject (*Trans. Chem. Soc.*, 1902, p. 321; *CHEMICAL NEWS*, vol. lxxxv., p. 271 *et seq.*) it was shown that a constituent responsible for part of the radio-activity of thorium could be separated from its compounds by chemical means. Two methods were given. In one a thorium solution was precipitated by ammonia, and the thorium hydroxide precipitate showed only about one-third of the normal activity, while the filtrate on evaporation and removal of the ammonium salts by ignition left a very active residue—in some cases over a thousand times as active as an equal weight of thoria. In the other method, thorium oxide was washed repeatedly with large quantities of water. The washings on evaporation deposited very active residues, while the radio-activity of the thoria was appreciably diminished by the process.

In both of these methods the active residues are extremely small, and the view was put forward that even the most active specimens consisted largely of accidental impurities, ThX—the active constituent of thorium—being only present in minute amount. By the kindness of Dr. Knöfler, of Berlin, who in the friendliest manner placed at our disposal a large specimen of his purest thorium nitrate, we were at once able to confirm this opinion. This specimen, which had been purified by a great many processes, did not contain any of the impurity precipitable by sodium phosphate after the removal of the thorium with ammonia, which was present in the commercial nitrate before used. The radio-activity and emanating power of Dr. Knöfler's specimen were, however, at least as great as any other in our possession, and the residues obtained from the filtrate after precipitating with ammonia were no less active.

1. Scope of the Present Paper.

In the present communication the results of a further detailed investigation of the radio-activity and emanating power of thorium compounds are given, and these have led to a theoretical interpretation of the processes involved which give rise to the phenomenon of natural radio-activity.

The Influence of Time on the Activity of Thorium and ThX.—The preparations employed in our previous experiments were allowed to stand over during the Christmas vacation. On examining them about three weeks later it was found that the thorium hydroxide which had originally possessed only about 36 per cent of its normal activity had almost completely recovered the usual value. The active residues, on the other hand, prepared by both methods, had almost completely lost their original activity. The chemical separation effected was thus not permanent in character. At this time, M. Becquerel's paper (*Comptes Rendus*, cxxiii., p. 977, December 9, 1901) came to hand, in which he shows that the same phenomena of recovery and decay are presented by uranium after it has been partially separated from its active constituent by chemical treatment.

* Communicated by the Authors.

A long series of observations was at once started to determine:—

1. The rate of recovery of the activity of thorium rendered less active by removal of ThX;
2. The rate of decay of the activity of the separated ThX;

in order to see how the two processes were connected. The results led to the view that may at once be stated. The radio-activity of thorium at any time is the resultant of two opposing processes.

1. The production of fresh radio-active material at a constant rate by the thorium compound;
2. The decay of the radiating power of the active material with time.

The normal or constant radio-activity possessed by thorium is an equilibrium value, where the rate of increase of radio-activity due to the production of fresh active material is balanced by the rate of decay of radio-activity of that already formed. It is the purpose of the present paper to substantiate and develop this hypothesis.

2. The Rates of Recovery and Decay of Thorium Radio-activity.

A quantity of the pure thorium nitrate was separated from ThX in the manner described by several precipitations with ammonia. The radio-activity of the hydroxide so obtained was tested at regular intervals to determine the rate of recovery of its activity. For this purpose the original specimen of 0.5 gram. was left undisturbed throughout the whole series of measurements on the plate over which it had been sifted, and was compared always with 0.5 gram. of ordinary "de-emanated" thorium hydroxide spread similarly on a second plate, and also left undisturbed. The emanation from the hydroxide was prevented from interfering with the results by a special arrangement for drawing a current of air over it during the measurements.

The rate of rise of emanating power of the same preparation was determined at the same time (see Section 7). The methods and apparatus employed have already been described in the previous paper.

The active filtrate from the preparation was concentrated and made up to 100 c.c. volume. One quarter was evaporated to dryness, and the ammonium nitrate expelled by ignition in a platinum dish, and the radio-activity of the residue tested at the same intervals as the hydroxide to determine the rate of decay of its activity. The comparison in this case was a standard sample of uranium oxide kept undisturbed on a metal plate, which repeated work has shown to be a perfectly constant source of radiation. The remainder of the filtrate was used for other experiments (Sections 5 and 7).

The following table gives an example of one of a numerous series of observations made with different preparations at different times. The maximum value attained by the hydroxide and the original value of the ThX are taken as 100:—

Time in days.	Activity of hydroxide.	Activity of ThX.
0	44	100
1	37	117
2	48	100
3	54	88
4	62	72
5	68	—
6	71	53
8	78	—
9	—	29.5
10	83	25.2
13	—	15.2
15	—	11.5
17	96.5	—
21	99	—
28	100	—

Fig. 1 shows the curves obtained by plotting the radio-activities as ordinates, and the time in days as abscissæ.

Curve 2 illustrates the rate of recovery of the activity of thorium. Curve 1 the rate of decay of activity of ThX. It will be seen that neither of the curves is regular for the first two days. The activity of the hydroxide at first actually diminished, and was at the same value after two days as when first prepared. The activity of the ThX, on the other hand, at first increases, and does not begin to fall below its original value till after the lapse of two days (compare Section 8). These results cannot be ascribed to errors of measurement, for they have been regularly observed whenever similar preparations have been tested. The activity of the residue obtained from thorium oxide by the second method of washing decayed very similarly to that of ThX as shown by the above curve.

If for present purposes the initial periods of the curve are disregarded and the later portions only considered, it will be seen at once that the time taken for the hydroxide to recover one-half of its lost activity is about equal to the time taken by the ThX to lose half its activity, viz., in each case about four days, and, speaking generally, the percentage proportion of the lost activity regained by the hydroxide over any given interval is approximately equal to the percentage proportion of the activity lost by the ThX during the same interval. If the recovery curve is produced backwards in the normal direction to cut the vertical axis, it will be seen to do so at a minimum of about 25 per cent, and the above result holds even more accurately if the recovery is assumed to start from this constant minimum, as indeed it has been shown to do under suitable conditions (Section 8, Fig. 4). This is brought out by Fig. 2, which represents the recovery curve of thorium in which the percentage amounts of activity recovered, reckoned from this 25 per cent minimum, are plotted as ordinates. In the same figure the decay curve after the second day is shown on the same scale.

The activity of ThX decreases very approximately in a geometrical progression with the time, i.e., if I_0 represent the initial activity and I_t the activity after time t ,

$$\frac{I_t}{I_0} = e^{-\lambda t} \dots \dots \dots (1),$$

where λ is a constant and e the base of natural logarithms.

The experimental curve obtained with the hydroxide for the rate of rise of its activity from a minimum to a maximum value will therefore be approximately expressed by the equation—

$$\frac{I_t}{I_0} = 1 - e^{-\lambda t} \dots \dots \dots (2),$$

where I_0 represents the amount of activity recovered when the maximum is reached, and I_t the activity recovered after time t , λ being the same constant as before.

Now, this last equation has been theoretically derived in other places (compare Rutherford, *Phil. Mag.*, 1900, pp. 10 and 181) to express the rise of activity to a constant maximum of a system consisting of radiating particles in which:—

1. The rate of supply of fresh radiating particles is constant;
2. The activity of each particle dies down geometrically with the time according to equation (1).

It therefore follows that if the initial irregularities of the curves are disregarded and the residual activity of thorium is assumed to possess a constant value, the experimental curve obtained for the recovery of activity will be explained if two processes are supposed to be taking place:—

1. That the active constituent ThX is being produced at a constant rate;
2. That the activity of the ThX decays geometrically with time.

Without at first going into the difficult questions connected with the initial irregularities and the residual activity, the main result that follows from the curves given can be put to experimental test very simply. The primary conception is that the major part of the radio-

activity of thorium is not due to the thorium at all, but to the presence of a non-thorium substance in minute amount which is being continuously produced.

3. Chemical Properties of ThX.

The fact that thorium on precipitation from its solutions by ammonia leaves the major part of its activity in the filtrate, does not of itself prove that a material constituent responsible for this activity has been chemically separated. It is possible that the matter constituting the non-thorium part of the solution is rendered temporarily radio-active by its association with thorium, and this property is retained through the processes of precipitation, evaporation, and ignition, and manifests itself finally on the residue remaining.

This view, however, can be shown to be quite untenable, for upon it any precipitate capable of removing thorium completely from its solution should yield active residues similar to those obtained from ammonia. Quite the reverse, however, holds.

When thorium nitrate is precipitated by sodium or ammonium carbonate, the residue from the filtrate by evaporation and ignition is free from activity, and the thorium carbonate obtained possesses the normal value for its activity.

The same holds true when oxalic acid is used as the precipitant. This reagent, even in strongly acid solution, precipitates almost all of the thorium. When the filtrate is rendered alkaline by ammonia, filtered, evaporated, and ignited, the residue obtained is inactive.

In the case where sodium phosphate is used as the precipitant in ordinary acid solution, the part that comes down is more or less free from ThX. On making the solution alkaline with ammonia, the remainder of the thorium is precipitated as phosphate, and carries with it the whole of the active constituent, so that the residue from the filtrate is again inactive.

In fact, ammonia is the only reagent of those tried capable of separating ThX from thorium.

The result of Sir William Crookes with uranium, which we have confirmed working with the electrical method, may be here mentioned. UrX is completely precipitated by ammonia, together with the uranium, and the residue obtained by the evaporation of the filtrate is quite inactive.

There can thus be no question that both ThX and UrX are distinct types of matter with definite chemical properties. Any hypothesis that attempts to account for the recovery of activity of thorium and uranium with time must of necessity start from this primary conception.

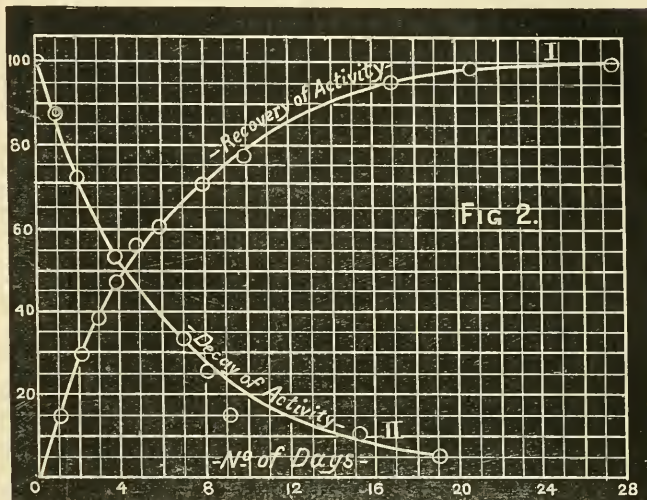
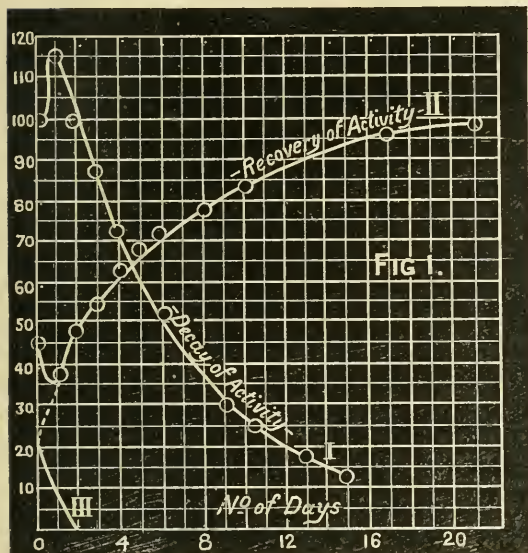
4. The Continuous Production of ThX.

If the recovery of the activity of thorium with time is due to the production of ThX, it should be possible to obtain experimental evidence of the process. The first point to be ascertained is how far the removal of ThX by the method given reduces the total radio-activity of thorium. A preliminary trial showed that the most favourable conditions for the separation was by precipitating in hot dilute solutions by dilute ammonia. A quantity of 5 grms. of thorium nitrate, as obtained from the maker, was so precipitated by ammonia, the precipitate being re-dissolved in nitric acid, and re-precipitated under the same conditions successively *without lapse of time*. The removal of ThX was followed by measuring the activity of the residues obtained from the successive filtrates. The activity of the ThX from the first filtrate was equivalent to 4.23 grms. of thoria, from the second to 0.33 grm., and from the third to 0.07 grm. It will be seen that by two precipitations the whole of the ThX is removed. The radio-activity of the separated hydroxide was 48 per cent of that of the standard de-emanated sample of thoria.

Rate of Production of ThX.—A quantity of thorium nitrate solution, that had been freed from ThX about a month before, was again subjected to the same process.

The activity of the residue from the filtrate in an experiment in which 10 grms. of this nitrate had been employed was equivalent to 8.3 grms. of thorium oxide. This experiment was performed on the same day as the one recorded above, in which 5 grms. of new nitrate had been employed, and it will be seen that there is no difference in the activity of the filtrates in the two cases. In one month

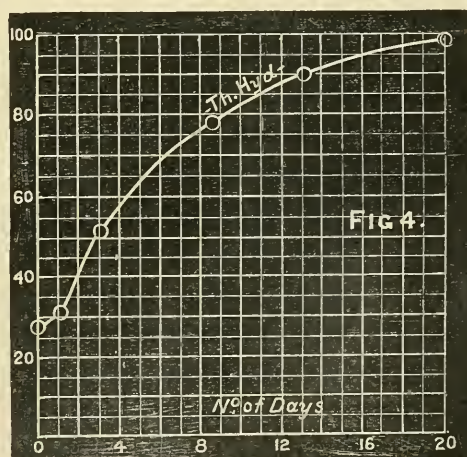
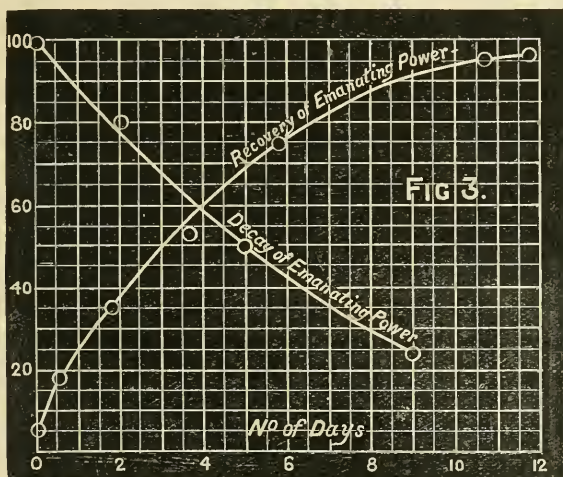
effed, the course of production of ThX can be followed after extremely short intervals. Working with 10 grms. of thorium nitrate, the amount produced in the minimum time taken to carry out the successive precipitations is as much as can be conveniently measured. If any interval is allowed to elapse the effect is beyond the range of the instrument, unless the sensitiveness is



the activity of the ThX in a thorium compound again possesses its maximum value.

If a period of two hours is allowed to elapse between the successive precipitations, the activity of the ThX formed during that time corresponds to about one-sixth of the maximum activity of the total thorium employed. In three hours the activity of the amount produced is about one-thirtieth. The rate of production of ThX worked out

reduced to a fraction of its ordinary value by the introduction of capacities into the system. Capacities of 0.01 and 0.02 microfarad, which reduce the sensitiveness to less than one-hundredth and one two-hundredth of the normal, were frequently employed in dealing with these active residues. For ordinary work with 0.25 to 0.5 gram. of thorium compound 0.001 microfarad was necessary. Most of the measurements in the course of the present paper



from these figures well agrees with the form of the curve obtained for the recovery of activity of thorium, if the latter is taken to express the continuous production of ThX at a constant rate and diminution of the activity of the product in geometrical progression with the time.

By using the Dolezalek electrometer, on which the radio-activity of 1 m.grm. of thorium produces a measureable

were made with this instrument, and a range from that represented by 1 m.grm. of thorium to any desired maximum could readily be obtained. Of course the greatest care is necessary in working with so sensitive an instrument to prevent electrostatic disturbances of every kind.

The process of the production of ThX is continuous, and no alteration was observed in the amount produced in a

given time after repeated separations. In an experiment carried out for another purpose (Section 8) after twenty-three successive precipitations extending over nine days, the amount formed during the last interval was, as far as could be judged, no less than what occurred at the beginning of the process.

The phenomenon of radio-activity, by means of the electrometer as its measuring instrument, thus enables us to detect and measure changes occurring in matter after a few minutes interval, which have never yet been detected by the balance or suspected of taking place.

5. Influence of Conditions on the Changes occurring in Thorium.

It has been shown that in thorium compounds the decay of radio-activity with time is balanced by a continuous production of fresh active material. The change which produces this material must be chemical in nature, for the products of the action are different in chemical properties from the thorium from which they are produced. The first step in the study of the nature of this change is to examine the effect of conditions upon its rate.

Effect of Conditions on the rate of Decay.—Since the activity of the products affords the means of measuring the amount of change, the influence of conditions on the rate of decay must first be found. It was observed that like all other types of temporary radio-activity the rate of decay is unaltered by any known agency. It is unaffected by ignition and chemical treatment, and the material responsible for it can be dissolved in acids, and re-obtained by the evaporation of the solution without affecting the activity. The following experiment shows that the activity decays at the same rate in solutions as in the solid state:—The remainder of the solution that had been used to determine the decay curve of ThX (Fig. 1) was allowed to stand, and at the end of twelve days a second quarter was evaporated to dryness and ignited, and its activity compared with that of the first, which had been left since evaporation upon its original platinum dish. The activities of the two specimens so compared with each other was indistinguishable, showing that in spite of the very different conditions the two fractions had decayed at equal rates. After nineteen days a third quarter was evaporated, and the activity, now very small, was indistinguishable from that of the fraction first evaporated. Re-solution of the residue after the activity had decayed does not at all regenerate it. The activity of ThX thus decays at a rate independent of the chemical and physical condition of the molecule.

Therefore the rate of recovery of activity under different conditions in thorium compounds affords a direct measure of the rate of production of ThX under these conditions. The following experiments were performed:—

One part of thorium hydroxide newly separated from ThX was sealed up in a vacuum obtained by a good Töpler pump, and the other part exposed to air. On comparing the samples twelve days later, no difference could be detected between them either in their radio-activity or emanating power.

In the next experiment a quantity of hydroxide freed from ThX was divided into two equal parts; one was exposed for twenty hours to the heat of a Bunsen burner in a platinum crucible, and then compared with the other. No difference in the activities was observed. In a second experiment one-half was ignited for twenty minutes on the blast, and then compared with the other with the same result. The difference of temperature and the conversion of thorium hydroxide into oxide thus exercised no influence on the activity.

Some experiments that were designed to test in as drastic a manner as possible the effect of the chemical condition of the molecule on the rate of production of ThX brought to light small differences, but these are almost certainly to be accounted for in another way. It will be shown later (Section 8) that about 21 per cent of the normal radio-activity of thorium oxide under ordinary con-

ditions consists of a secondary activity excited on the mass of the material. This portion is of course a variable, and since it is divided among the total amount of matter present, the conditions of aggregation, &c., will affect the value of this part. This effect of excited radio-activity in thorium makes a certain answer to the question difficult, and on this account the conclusion that the rate of production of ThX is independent of the molecular conditions is not final. The following experiment, however, makes it extremely probable:—

A quantity of thorium nitrate as obtained from the maker was converted into oxide in a platinum crucible by treatment with sulphuric acid and ignition to a white heat. The de-emanated oxide so obtained was spread on a plate, and any change in radio-activity with time, which under these circumstances could certainly be detected, was looked for during the first week from preparation. None whatever was observed, whereas if the rate of production of ThX in thorium nitrate is different from that in the oxide, the equilibrium point at which the decay and increase of activity balance each other will be altered in consequence. There should have therefore occurred a logarithmic rise or fall from the old to the new value. As, however, the radio-activity remained constant, it appears very probable that the changes involved are independent of the molecular condition. It will be seen that the assumption is here made that the proportion of excited radio-activity in the two compounds is the same, and for this reason compounds were chosen which possess but low emanating power. (Compare Section 7, last paragraph).

Uranium is a far simpler example of a radio-active element than thorium, as the phenomena of excited radio-activity and emanating power are here absent. The separation of UrX and the recovery of the activity of the uranium with time appear, however, analogous to these processes in thorium, and the rate of recovery and decay of uranium activity are at present under investigation. It is proposed to test the influence of conditions on the rate of change more thoroughly in the case of uranium, as here secondary changes do not interfere.

6. The Cause and Nature of Radio-activity.

The foregoing conclusions enable a great generalisation to be made in the subject of radio-activity. Energy considerations require that the intensity of radiation from any source should die down with time unless there is a constant supply of energy to replace that dissipated. This has been found to hold true in the case of all known types of radio-activity with the exception of the "naturally" radio-active elements—to take the best established cases, thorium, uranium, and radium. In their first paper on the present subject, the authors showed that the radio-activity of the emanation produced by thorium compounds decayed geometrically with the time under all conditions, and was not affected by the most drastic chemical and physical treatment. The same has been shown by one of us (*Phil. Mag.*, 1900, p. 161) to hold for the excited radio-activity produced by the thorium emanation. This decays at the same rate whether on the wire on which it is originally deposited, or in solution of hydrochloric or nitric acid. The excited radio-activity produced by the radium emanation appears analogous. All these examples satisfy energy considerations. In the case of the three naturally occurring radio-active elements, however, it is obvious that there must be a continuous replacement of the dissipated energy, and no satisfactory explanation has yet been put forward.

The nature of the process becomes clear in the light of the foregoing results. The material constituent responsible for the radio-activity, when it is separated from the thorium which produces it, then behaves in the same way as the other types of radio-activity cited. Its activity decays geometrically with the time, and the rate of decay is independent of the molecular conditions. The normal radio-activity is, however, maintained at a constant value by a chemical change which produces fresh radio-active

material at a rate also independent of the conditions. The energy required to maintain the radiations will be accounted for if we suppose that the energy of the system after the change has occurred is less than it was before.

The work of Crookes and Becquerel on the separation of Urx and the recovery of the activity of the uranium with time, makes it appear extremely probable that the same explanation holds true for this element. The work of M. and Mme. Curie, the discoverers of radium, goes to show that this body easily suffers a temporary decrease of its activity by chemical treatment, the normal value being regained after the lapse of time, and this can be well interpreted on the new view. All known types of radio-activity can thus be brought under the same category.

(To be continued).

ON THE FERROCYNANIDES OF CADMIUM.*

By EDMUND H. MILLER.

It has already been shown (Miller and Fisher, *Journ. Amer. Chem. Soc.*, September, 1900) that the results obtained in titrating cadmium by potassium ferrocyanide in a neutral or slightly acid solution do not agree with any of the formulæ given for the precipitate, while the values obtained in an ammoniacal solution agree very closely with the formula $\text{K}_2\text{CdFe}(\text{CN})_6$.

The present work was undertaken to study the variation in composition under different conditions, and, if possible, to assign definite formulæ to the precipitates so formed. To cover the ground as completely as possible, the following series of precipitates were made:—

- A.—Neutral solution, cadmium in excess.
- B.—Neutral solution, ferrocyanide in excess.
- C.—Acid with hydrochloric, 10 c.c. (sp. gr. 1.20) per litre, cadmium in excess.
- D.—Acid with hydrochloric, 10 c.c. (sp. gr. 1.20) per litre, ferrocyanide in excess.
- E.—Acid with acetic, 10 c.c. 50 per cent acetic acid per litre, cadmium in excess.
- F.—Acid with acetic, 10 c.c. 50 per cent acetic acid per litre, ferrocyanide in excess.
- G.—Alkaline with ammonia, † cadmium in excess.
- H.—Alkaline with ammonia, † ferrocyanide in excess.

The precipitates were all formed in large beakers, in the cold, and allowed to stand, then washed with water, water containing hydrochloric acid, water containing acetic acid, water and ammonia, respectively, so that the conditions of precipitation were maintained, then washed with water till free from excess of cadmium or of ferrocyanide. The work was begun in June, 1900, and the precipitates analysed a year later.

In general, whenever the cadmium was in excess the precipitates settled well, and when ferrocyanide was in excess, very badly. The salts used for this series of precipitations were cadmium nitrate and potassium ferrocyanide.

The method of analysis was in all cases the same, and the object was to obtain the ratio between iron and potassium and cadmium. Some attempts were made at first to dry the precipitates to constant weight, but as decomposition resulted no attempt was made to weigh the portions taken for analysis, but all the determinations were expressed as ratios.

The precipitates were repeatedly evaporated in casserole with nitric and sulphuric acids till decomposition was complete, the residue was dissolved in water, the excess of sulphuric acid neutralised with ammonia, and the cadmium precipitated as sulphide in a very weak

hydrochloric acid solution, dissolved and determined as phosphate (Miller and Page, *School of Mines Quarterly*, July, 1901, and *Zeit. Anorg. Chem.*, 1901, xxviii., 233). In the filtrate the iron was, after oxidation, precipitated as hydroxide and weighed as ferric oxide. The filtrate from the iron was evaporated, the ammonium salts expelled, and the potassium weighed as sulphate. In the determination of cadmium as phosphate, weighing as pyrophosphate, and as cadmium ammonium phosphate, $(\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O})$, were tried, and the weighing as cadmium ammonium phosphate adopted as more convenient.

The following is a brief description of the precipitates formed and the results obtained from their analysis expressed as an atomic ratio* :—

A (neutral solution, cadmium in excess).—Yellowish-white, settled well, was washed (nine times) till free from cadmium; when dry, was yellowish-white, apparently slightly oxidised to ferricyanide. Gave, on analysis, $\text{Fe}:\text{K}:\text{Cd}::1:1.14:1.42$ or $7:8:10$, corresponding to $\text{K}_8\text{Cd}_{10}[\text{Fe}(\text{CN})_6]_7$.

B (neutral, ferrocyanide in excess).—White, settled partially after five months, was washed at intervals for a year. It was the most tedious of all, but did not give evidence of decomposition. The ratio was $\text{Fe}:\text{K}:\text{Cd}::1:1.80:1.08$.

C (hydrochloric, cadmium in excess).—Dull orange-yellow, settled very well; on washing with water containing 10 c.c. concentrated hydrochloric acid per litre, the supernatant liquid became greenish with evident decomposition of the precipitate. A second lot was made under the same conditions; the precipitate, at first white, became yellow within a few seconds. The yellow precipitate is also formed when cadmium is dissolved in hydrochloric and a little nitric acid, then neutralised, 2 c.c. of hydrochloric acid added, and then titrated by potassium ferrocyanide. It is not due to the presence of any nitroprusside, and is undoubtedly due to the oxidation of part of the cadmium ferrocyanide to ferricyanide, which is brownish-yellow, by the nitrate present in both cases. This precipitate was not analysed.

D (hydrochloric, ferrocyanide in excess).—The precipitate, at first yellowish, became white when an excess of potassium ferrocyanide was present; it settled quite well at first, but badly after washing, like the others when an excess of ferrocyanide is present, and showed a greenish-yellow colour after washing, evidently due to a slight decomposition. The results were $\text{Fe}:\text{K}:\text{Cd}::1:1.933:0.991$, corresponding to $\text{K}_2\text{CdFe}(\text{CN})_6$.

E (acetic, cadmium in excess).—The precipitate was nearly white, settled well, and on drying was white. The ratio was $\text{Fe}:\text{K}:\text{Cd}::1:1.21:1.392$, corresponding quite closely to $\text{K}_6\text{Cd}_7[\text{Fe}(\text{CN})_6]_5$.

F (acetic, cadmium in excess).—Creamy white precipitate which settled badly, and on drying was slightly greenish on the surface. The iron cadmium ratio was 1:0.95, corresponding approximately to $\text{K}_2\text{CdFe}(\text{CN})_6$.

G (ammonia, cadmium in excess).—A pure white precipitate which gave considerable trouble in testing for an excess of cadmium, as owing to the excess of cadmium dissolved in ammonia, a point was reached where either FeCN_6''' or Cd'' ions gave a precipitate. The precipitate on washing became flocculent, and settled immediately; it was washed six times with water containing ammonia, and then with water until no test for cadmium was obtained. The analytical results gave the ratio $\text{Fe}:\text{K}:\text{Cd}::1:0.3:3.33$, a result impossible for a ferrocyanide. After re-washing with strong ammonia to dissolve out the excess of cadmium, which was undoubtedly present as either hydroxide or carbonate, and which gave the flocculent character to the precipitate, the ratio be-

* Contribution from the Havemeyer Laboratories, Columbia University. From the *Journal of the American Chemical Society*, xxiv., No. 3.

† The cadmium hydroxide was dissolved in an excess of ammonia before the potassium ferrocyanide was added.

* These values are obtained by dividing the calculated weights of iron, potassium, and cadmium, by their atomic weights, and then multiplying by $\frac{1}{\text{wt. iron}}$.

came Fe: Cd :: 1:1.04, agreeing approximately with the normal ferrocyanide, $\text{Cd}_2\text{Fe}(\text{CN})_6$.

H (ammonia, ferrocyanide in excess).—Pure white precipitate which settles well at first, but poorly after washing.* In this case only, the iron cadmium ratio was determined; the figures obtained were 1:0.97, corresponding to $\text{K}_2\text{CdFe}(\text{CN})_6$.

On account of the oxidation and decomposition of some of the precipitates just described, a second set of eight was made under exactly the same conditions, using cadmium chloride instead of nitrate. These were made in December, 1900, and are marked A', B', &c., so as to be readily compared with the preceding series.

A' (neutral, cadmium in excess).—White precipitate, which settled well, and was completely washed in a month. On analysis, the ratio found was Fe:K: Cd :: 1:1.14: 1.448 or 7:8:10, agreeing with the results obtained in A and the formula $\text{K}_8\text{Cd}_{10}[\text{Fe}(\text{CN})_6]_7$.

B' (neutral, ferrocyanide in excess).—A slightly yellowish precipitate which did not settle at all; various methods were tried to hasten the settling, but without effect, so it was finally abandoned.

C' (hydrochloric, cadmium in excess).—White precipitate which settled well, gave iron to cadmium 1:1.46 1:1.44. Results very similar to those obtained from A, and agreeing with a ratio of Fe:K: Cd of 7:8:10.

D' (hydrochloric, ferrocyanide in excess).—A greenish precipitate which would not settle. Separation by a centrifugal was tried as well as other methods, such as the addition of sodium chloride but without effect; finally it became so decomposed as to be worthless.

E' (acetic, cadmium in excess).—White, settled well, leaving a turbid solution; gave, on analysis, Fe:K: Cd :: 1:1.078: 1.383.

F' (acetic, ferrocyanide in excess).—This precipitate became very green on standing, and was rejected.

G' (ammonia, cadmium in excess).—A perfectly white curdy precipitate which settles immediately, leaving a clear colourless liquid, and differs entirely in physical properties from the preceding. It gave, on analysis, the ratio 1:0:2.27, showing, as in G, no potassium, and the presence of cadmium in excess of the possible ratio for a ferrocyanide.

H' (ammonia, ferrocyanide in excess).—A creamy white precipitate which settles well and has the consistency of clay, requiring considerable force to stir it up, and differing entirely in physical properties from the others. It gave, on analysis, Fe:K: Cd :: 1:2.07: 1.048 or nearly 1:2:1, corresponding to $\text{K}_2\text{CdFe}(\text{CN})_6$.

It remained to obtain precipitates to take the places of B', D', and F'. So in March, 1901, these precipitates were made again under the conditions already described, but in dark brown glass bottles, and were kept in the dark. This greatly lessened the decomposition, and by sacrificing a large proportion of the precipitates with the wash-water by July, residues were obtained which were free from excess of ferrocyanide, and only slightly bluish in colour.

B'' (neutral, ferrocyanide in excess).—Ratio, 1:1.81: 1.12, agreeing fairly with B and with $\text{K}_{18}\text{Cd}_{11}[\text{Fe}(\text{CN})_6]_{10}$.

D'' (hydrochloric, ferrocyanide in excess).—Ratio, 1:2.02: 0.955, confirming D, and corresponding to $\text{K}_2\text{CdFe}(\text{CN})_6$.

F'' (acetic, ferrocyanide in excess).—Ratio, 1:2.03: 0.95, confirming F, and corresponding to $\text{K}_2\text{CdFe}(\text{CN})_6$.

The abnormal results in G and G', probably due to cadmium hydroxide being carried down in varying quantities, necessitated a repetition of this work, so in July, 1901, G'' was made under the same conditions, but was treated repeatedly with very large quantities of ammonia before washing with water, and then analysed at once.

G''' (ammonia, cadmium in excess).—The iron cadmium ratio was determined in duplicate, and found to be 1:1.496, corresponding to $\text{K}_2\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$.

When this precipitate was being washed it was noticed that there was a portion which did not settle as well as the rest; this was decanted from the part which settled well, washed, and analysed, giving a ratio of exactly 1Fe: 1Cd.

In the results already given the duplicates on C' and the ratios on E and E' did not check satisfactorily, so these precipitates were made again (July, 1901), and as they settled well (cadmium being in excess) they were washed and analysed within a week.

C''' (hydrochloric, cadmium in excess).—White, no decomposition; gave Fe: Cd :: 1:1.07 and 1:1.065.

E''' (acetic, cadmium in excess).—White, no decomposition; gave Fe: Cd :: 1:1.07 and 1:1.06.

We see in these two a total lack of agreement in composition with those which were allowed to stand many months before analysis, indicating a change in composition after precipitation. On the other hand, these last results are in exact agreement with the titration ratios in slightly acid solution (Miller and Fisher, *Journ. Amer. Chem. Soc.*, 1900, xxi., 542); for if the theory for $\text{K}_4\text{Fe}(\text{CN})_6$ or 1Fe: 1Cd* gives for the strength of the ferrocyanide solution 1 c.c. = 0.00671 grm. cadmium, then, if the ratio in the precipitate is 1:1.07, the strength of the solution in terms of cadmium becomes 1.07 x 0.00671 or 0.00718, while the average result of titration was 0.00717.

For ease of comparison let us disregard for the present the potassium, which has been found to be present always in the proper amount to satisfy the remaining valency of the ferrocyanogen radical, and consider only the iron cadmium ratios.

Character of solution.	Cadmium in excess.		Ferrocyanide in excess.	
	Fe: Cd.		Fe: Cd.	
Neutral	1:1.42	A	1:1.08	B
	1:1.448	A'	1:1.12	B''
Hydrochloric ..	1:1.462	C'	1:0.99	D
	1:1.44	C'	1:0.955	D''
	1:1.07	C''' (a)	—	—
	1:1.065	C''' (a)	—	—
Acetic	1:1.392	E	1:0.95	F
	1:1.383	E'	1:0.95	F''
	1:1.07	E''' (a)	—	—
	1:1.06	E''' (a)	—	—
Ammonia ..	1:3.33	G	1:0.97	H
	1:1.91	G (b)	1:1.048	H'
	1:1.94	G'	—	—
	1:2.27	G'	—	—
	1:1.496	G'''	—	—
	1:1.496	G'''	—	—
	1:1	G''' (c)	—	—

(a) Analysed within a week of precipitation.

(b) After treatment with ammonia.

(c) Decanted portion.

We see from the work described that:—

1. The results when ferrocyanide is in excess are entirely different from those where cadmium is in excess.

2. In either acid or ammoniacal solution, ferrocyanide being in excess, the ratio is 1 iron to 1 cadmium, or the precipitate is $\text{K}_2\text{CdFe}(\text{CN})_6$, while in a neutral solution the cadmium ratio is higher.

3. With cadmium in excess, in either neutral or hydrochloric acid solution, the final composition is the same, corresponding to $\text{K}_8\text{Cd}_{10}[\text{Fe}(\text{CN})_6]_7$, while in an acetic acid solution the final composition corresponds to $\text{K}_6\text{Cd}_7[\text{Fe}(\text{CN})_6]_5$.

4. With cadmium in excess, in an acid solution the composition alters on standing with an increase of cadmium in the ratio, but when freshly precipitated the ratio agrees exactly with the results by titration.

5. With cadmium in excess, in an ammoniacal solution the ratio exceeds the normal, but after washing with am-

* Washed six times with ammonia and water, then with water till free from ferrocyanide.

* Based on Hermann's formula, $\text{K}_2\text{CdFe}(\text{CN})_6$.

monia corresponds to $\text{Cd}_2\text{Fe}(\text{CN})_6$; when freshly precipitated and washed quickly with ammonia, the part which settles badly being removed by decantation, the composition agrees exactly with $\text{K}_2\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$, while the part decanted corresponds to $\text{K}_2\text{CdFe}(\text{CN})_6$.

6. The constancy of the final composition of these precipitates does not favour the theory that potassium ferrocyanide is merely dragged down.

The results obtained when cadmium was in excess in an ammoniacal solution were so extraordinary that they deserved further study. The precipitate G''' , $\text{K}_2\text{Cd}_3[\text{Fe}(\text{CN})_6]_2$, was treated seven times with strong ammonia (sp. gr. 0.90) to see whether a change could be effected by a difference in solubility in ammonia, as the $\text{K}_2\text{CdFe}(\text{CN})_6$ seemed the more soluble. In this way, a creamy white residue was obtained which gave, on analysis, $\text{Fe} : \text{Cd} :: 1 : 1.99$, showing $\text{Cd}_2\text{Fe}(\text{CN})_6$, which was also obtained in G after re-washing with ammonia.

This result, together with the fact that the portion first obtained by decantation when the precipitate was originally treated with ammonia, gave a ratio of $\text{Fe} : \text{Cd}$ of exactly 1:1 shows that the original precipitate can be resolved into the two simple ferrocyanides $\text{Cd}_2\text{Fe}(\text{CN})_6$ and $\text{K}_2\text{CdFe}(\text{CN})_6$, and affords important confirmation of the theory that these complicated precipitates are mixtures, advanced several years ago in connection with the ferrocyanides of zinc and manganese (*Journ. Amer. Chem. Soc.*, 1897, xix., 556).

Now, if this is true for the precipitate in an ammoniacal solution, it ought also to be true of those more complicated ones formed in acid solutions; accordingly, C''' , which gave 1:1.07 when freshly precipitated, was treated in the same way with strong ammonia, and the residual cream-coloured portion analysed. This gave a ratio of 1:1.90, showing that the same change had taken place, though it was not entirely complete.

To test this further, precipitate A (neutral, cadmium in excess, made June, 1900) was treated eight times with strong ammonia and the residue analysed. This gave the ratio of 1:1.99, agreeing almost perfectly with $\text{Cd}_2\text{Fe}(\text{CN})_6$.

In order to ascertain whether the change which takes place on standing can be hastened by heating, the precipitate E''' (acetic, cadmium in excess), which when washed quickly and analysed gave a ratio of 1:1.07, was heated with water containing acetic acid on a water-bath for three days, and then analysed. The result was $\text{Fe} : \text{Cd} :: 1 : 1.40$ compared with 1:1.383 (E') after standing six months in the cold and 1:1.392 (E) after one year.

This precipitate (E''' after heating) was next treated eight times with strong ammonia, and the residual portion analysed. The result was $\text{Fe} : \text{Cd} :: 1 : 1.97$, showing again the presence of the normal cadmium ferrocyanide.

These experiments show that the ferrocyanides undergo a change in composition after precipitation, which progresses to the same point under the same conditions, and which is hastened by heating. The action of ammonia on these precipitates (cadmium in excess) has been confirmatory of the idea that they are either mixtures or else very easily decomposable double salts made up of $\text{K}_2\text{CdFe}(\text{CN})_6$ and $\text{Cd}_2\text{Fe}(\text{CN})_6$.

Written in this way the results are expressed as follows:—

Character of Solution : Neutral.

Cadmium in excess .. $4\text{K}_2\text{CdFe}(\text{CN})_6 \cdot 3\text{Cd}_2\text{Fe}(\text{CN})_6$
Ferrocyanide in excess $9\text{K}_2\text{CdFe}(\text{CN})_6 \cdot \text{Cd}_2\text{Fe}(\text{CN})_6$

Character of Solution : Hydrochloric.

Cadmium in excess .. $14\text{K}_2\text{CdFe}(\text{CN})_6 \cdot \text{Cd}_2\text{Fe}(\text{CN})_6$ (a)
Ferrocyanide in excess $\text{K}_2\text{CdFe}(\text{CN})_6$
Cadmium in excess .. $4\text{K}_2\text{CdFe}(\text{CN})_6 \cdot 3\text{Cd}_2\text{Fe}(\text{CN})_6$

Character of Solution : Acetic.

Cadmium in excess .. $14\text{K}_2\text{CdFe}(\text{CN})_6 \cdot \text{Cd}_2\text{Fe}(\text{CN})_6$ (a)
Ferrocyanide in excess $\text{K}_2\text{CdFe}(\text{CN})_6$
Cadmium in excess .. $3\text{K}_2\text{CdFe}(\text{CN})_6 \cdot 2\text{Cd}_2\text{Fe}(\text{CN})_6$

Character of Solution : Ammonia.

Cadmium in excess .. $\text{K}_2\text{CdFe}(\text{CN})_6 \cdot \text{Cd}_2\text{Fe}(\text{CN})_6$ (a)
Ferrocyanide in excess $\text{K}_2\text{CdFe}(\text{CN})_6$
(a) Freshly precipitated.

It would be premature to advance these formulæ as representing relations of these complicated and variable precipitates, but the facts seem to warrant this as a working hypothesis, to be used in a further study of the other insoluble ferrocyanides.

Although the results are not all that are desired, many of the precipitates are so easily oxidised, readily decomposed, and impossible to filter, that it seemed very doubtful whether any better results could be obtained if the work were repeated.

On comparing the results obtained on cadmium with those on zinc previously published (*Journ. Amer. Chem. Soc.*, 1897, xix., 547), and with those of Stone and Van Ingen (*Journ. Amer. Chem. Soc.*, 1897, xix., 542) we see some cases of remarkable agreement as well as some discrepancies, but a discussion of these results is postponed, as it is proposed to continue this work by a similar investigation of the ferrocyanides of the other metals of the periodic group containing cadmium and zinc, and also of the analytical group containing zinc, manganese, nickel, and cobalt, so that, taking zinc as a starting-point, we can see whether the variations in composition have any connection with the analytical grouping or the periodic law, and also possibly obtain more knowledge of their constitution.

THE CLASSIFICATION OF THE ELEMENTS.*

By HENRY E. ARMSTRONG, V.P.R.S.

(Concluded from p. 88).

It is unnecessary to go into further details—the table is self-explanatory; but it may not be superfluous to point out that the characteristic and most remarkable feature brought out by this mode of classifying the elements is the existence in various parts of the system of groups or series of related elements from the highest term of which alone "progression" takes place. The existence of such groups in the case of the iron and platinum metals and some of the rare earths, has long been recognised—but not their significance. It is not unlikely that some of the columns will be "cleared" of such groups when atomic weights generally are known with a closer approach to certainty. Of their existence in column 4, there can be no doubt; but if in column 7 rubidium were put at 84, 85 could be transferred to column 8; and if lower down in the same column, caesium were put at 131, 132 and 133 could be transferred to column 8, or the necessary "correction" might be made perhaps with greater advantage by including in column 4 two terms (81 and 82) in the fifth, and three (128, 129, 130) in the seventh period: column 7 would then be free from "grouped" elements. Such groups, however, are undoubtedly as characteristic of column 8 as of column 4; whether they are of column 9 is open to question—the cerium group might well follow barium in column 8; but wherever they may come, it is clear that the elements of this group are a very numerous body, and that a remarkable expansion may be looked forward to in this part of the table. Column 11 might also, by a similar process, be cleared of grouped elements. If such a clearance turn out to be possible, grouped elements will be characteristic of only three of the families—those in columns 4, 8, and 12.

Making allowances in the manner suggested, the "smoothed" scheme is arrived at which is embodied in Table II.

The possibilities disclosed by a system of classification such as that here suggested are remarkable, but they are on the surface and need not be dwelt upon. Speculation

* A Paper read before the Royal Society, March 20, 1902.

TABLE II.

1 H 17 33	2 He 18 34	3 F 19 35 Cl	4 A 20 36	5 21 37	6 22 38	7 Li 23 Na 39 K	8 Mg 24 40 Ca	9 Be 25 41	10 Ne 26 42 Kr	11 B 27 Al 43 Sc	12 C 28 Si 44 45 46 47 Ti 48	13 29	14 N 30	15 P 31	16 O 32 S
53	54	55 Mn	56 Fe 57 58 59 Co Ni	60	61	62	63 Cu 64 65 Zn 66	67	68 X	69 Ga	70 71 Ge 72 73	74	75 As	76	77 Se
78	79	80 Br	81 82	83	84	85 Rb	86 87 Sr	88	89	90 Yt	91 Zr 92	93	94	95 Nb	96 Mo
97	98	99	100 101 102 Ru 103 Rh 104 105 Pd	106	107	108 Ag	109 110 111 112 Cd	113	114	115 In	116 117 Va(?) 118 Sn 119 120	121 Sb	122	123	124 Te
125	126	127 I	128 129 130	131	132	133 Cs	134 135 136 Ba 137 138 La 139 140 Ce 141 Pr 142 143 144 Nd 145 146 147 148 149 150 Sm								

151 Eu

185	186	187	188 189 190 191 Os 192 193 Ir 194 Pt	195	196	197 Au	198 199 200 Hg 201	171	172	173 Yb	174 175 176 177 178 179 180	181	182	183 Ta	184 W
212	213	214	215 216 217 218 219 220	221	222	223	224 225 226 227 228	229	230	231	232 Th 233 234 235 236	237	238	239	240 U

on such a subject will be justified if it but lead to further appreciation of the rhythm which undoubtedly underlies the relationship subsisting among the elements. That work in plenty is left for the chemist to do is certain.

THE VOLUMETRIC ESTIMATION OF ALUMINA, AND FREE AND COMBINED SULPHURIC ACID IN ALUMS.*

By ALFRED H. WHITE.

In judging the quality of an alum, among the important determinations are those which give the amount of soluble alumina and the amount of sulphuric acid in combination with it or existing as free acid. The alumina may be satisfactorily estimated gravimetrically, but the method is tedious. A gravimetric estimation of the sulphuric acid gives not only that combined with aluminum plus that present as free sulphuric acid, but also that present as sodium sulphate, &c., and the amount of alkalis must be known before the amount of sulphuric acid combined with aluminum can be determined.

The determination of free sulphuric acid in alums by volumetric means has been repeatedly attempted. The hydrolysis of aluminum sulphate prevents direct titration with an alkali, since as fast as the free acid present is neutralised, more is formed by hydrolysis, so that the solution will not remain neutral for an appreciable length of time until nearly all the acid originally combined with the aluminum has been neutralised, and most of the aluminum hydroxide precipitated. This cannot be made into a practicable quantitative method for the estimation of free and combined acid, as the formation of aluminate with alkaline reaction begins before all the hydroxide has been precipitated. Further, if phenolphthalein is used as indicator, the precipitated hydroxide obstinately holds, by adsorption, the pink colour even when the solution is no longer alkaline, so that the method—though perhaps giving in the hands of works chemists in constant practice results which are fairly concordant—is, because of these various errors, not to be considered a practicable analytical method. The following paper results from an attempt to work out a practicable method.

A standard solution of barium hydroxide was used instead of caustic soda, to avoid any trouble caused by carbon dioxide in the caustic affecting the phenolphthalein used as indicator. It was found later that the barium hydroxide possessed other advantages. To prevent the adsorption of pink colour by the precipitated aluminum hydroxide obscuring the end-reaction, an addition of neutral potassium-sodium tartrate (Rochelle salt) was made to hold the alumina in solution. The modification proved a good one. Duplicate results checked closely. There was no precipitation of alumina during the titration, nor even of barium sulphate. The solution remained perfectly clear and colourless until the end-reaction, which was sharp. After standing a short time the solution became opalescent, and then milky, but no precipitate settled out. This marked retardation of the precipitation of barium sulphate was unexpected, and the conditions under which it occurs are undergoing further investigation.

To determine that the results thus obtained were accurate, a solution of aluminum sulphate was made by precipitating aluminum hydroxide from a solution of aluminum chloride with ammonia, washing the precipitate thoroughly, and then dissolving in standard sulphuric acid, which was afterward diluted to a litre (Solution A). The solution thus obtained was almost fifth normal, and the amount of acid was slightly in excess of the amount theoretically necessary to form the normal aluminum sulphate. A duplicate solution of acid

alone, carefully standardised gravimetrically, was used to check the results.

The method of procedure was as follows:—To 25 c.c. of the fifth-normal alum solution was added 50 c.c. of 10 per cent neutral potassium-sodium tartrate, and the mixture was titrated cold with barium hydroxide solution, using phenolphthalein as indicator. This amount of tartrate was sufficient to prevent anything more than a slight opalescence in the solution before the end-reaction. Duplicate titrations required 25.85 and 25.80 c.c. of fifth-normal barium hydroxide. To determine the effect of the amount of tartrate, another titration was made, using 100 c.c. of tartrate instead of 50. The amount of barium hydroxide solution used was 25.85, as before. The check solution of sulphuric acid required 25.65 c.c. barium hydroxide, no difference being apparent whether no tartrate, 50 c.c., or 100 c.c. of tartrate were present. The solution containing the aluminum sulphate therefore requires slightly more barium hydroxide than that containing the sulphuric acid alone. A possible explanation is that the ionisation of the barium hydroxide is lessened to such an extent by the aluminum tartrate complex that it requires an appreciably large excess of barium hydroxide to bring about the end reaction. If, however, the barium hydroxide is standardised against a solution of aluminum sulphate made from precipitated alumina and sulphuric acid as described, the results will be constant and give accurate results when extended to other alums. The addition of sodium sulphate in amount equivalent to the amount of sulphuric acid combined with the aluminum does not affect the result; the addition of standard sulphuric acid increases the amount of barium hydroxide used by the theoretical amount. The addition of neutral tartrate and titration with barium hydroxide, therefore, affords an accurate method of determining the total sulphuric acid combined with the aluminum plus the excess of free acid, irrespective of the amount of sulphuric acid combined with alkalis.

As it is well known that the hydroxy-organic acids in general have the power of preventing the precipitation of alumina, salts of other acids than tartaric were tried, among them neutral sodium citrate. Sodium citrate prevented the precipitation of alumina, retarded the precipitation of barium sulphate, and allowed a perfectly sharp end-reaction, as did the tartrate, but the amount of barium hydroxide used was only a little over two-thirds of that required when titrating in the presence of the tartrate. Solution A, with neutral sodium citrate added, required only 17.95 c.c. barium hydroxide instead of 25.84 when tartrate was used. Experiment showed that the addition of sodium sulphate did not affect the result, and that an addition of standard sulphuric acid caused the theoretically calculated increase in the barium hydroxide used. It seemed that the result obtained when titrating in the presence of citrate could be due only to the formation of a complex aluminum ion, and that this might furnish the basis of a method for the estimation of the aluminum. If we assume that the barium hydroxide used when titrating in presence of tartrate, represents free acid plus acid combined with alumina, while the barium hydroxide used when titrating in presence of citrate represents free acid plus two-thirds of acid combined with alumina, the difference represents one-third of the sulphuric acid combined with the alumina, or one-third the alumina. In the above instance, $25.84 - 17.95 = 7.89$ c.c. fifth-normal barium hydroxide, and calculating the alumina on the assumption that this is equivalent to one-third of it, we find that we get 0.0805 gm. of alumina as compared with 0.0831 gm. obtained gravimetrically. The volumetric result is too low. It seemed entirely possible that partial hydrolysis of the alum in the citrate solution might cause more barium hydroxide to be used than called for by the above supposition, and that this might account for the low result. Accordingly, among other variations, the solution of aluminum sulphate was evaporated to dryness on the water-bath and dissolved in 50 c.c. of 10 per cent sodium citrate

* Contribution from the Chemical Laboratory of the University of Michigan. From the *Journal of the American Chemical Society*, xiv., No. 5.

and titrated. There were required only 17.58 c.c. barium hydroxide instead of 17.95 c.c., and the alumina calculated from this is 0.0842 gm. instead of 0.0831 gm. obtained gravimetrically. Using a saturated solution of citrate to re-dissolve the alum did not give an appreciably different result. Thus, the first method gives results considerably low, while the second gives slightly higher results. Some further experiments upon the influence of concentration and time follow, made upon a C. P. aluminum sulphate in a solution of 30 grms. per litre (Solution B).

B.	Volume aluminum sulphate.	Water added.	Citrate added.	Barium hydroxide.	Remarks.
1.	25	0	50	21.75	Titrated at once.
2.	25	25	50	21.76	Titrated at once.
3.	25	50	50	21.67	Water added; stood fifteen minutes; then citrate added, and titrated.
4.	25	100	50	21.70	Water added; stood fifteen minutes; then citrate added, and titrated.
5.	25	200	50	21.72	Water added; stood fifteen minutes; then citrate added, and titrated.
6.	25	Evaporated to dryness and re-dissolved in 50 c.c. 10 per cent citrate; stood ten minutes before titrating; required 21.62 c.c. barium hydroxide.			
7.	0.750 gram. (25 c.c.) of solid salt, dissolved in 50 c.c. 10 per cent citrate and titrated at once, required 21.90 c.c. barium hydroxide.				

The above series of experiments shows that the addition of varying amounts of water and variation of time within short intervals makes but slight difference in the result. The hydrolysis is apparently a slow one. In twenty-four hours, however, equilibrium is practically complete, as is shown by another series of experiments on a commercial aluminum sulphate dissolved to a strength of 30 grms. per litre (Solution C).

C.	Volume aluminum sulphate.	20 per cent citrate added.	Barium hydroxide.	Remarks.
1.	25	25	21.0	Titrated at once.
2.	25	25	21.02	Stood fifteen minutes before titrating.
3.	25	25	20.62	Stood sixteen hours before titrating.
4.	25	Evaporated to dry- ness and re-dis- solved in 50 c.c. 10 per cent ci- trate.	20.53	Titrated at once.
5.	25	Evaporated to dry- ness and re-dis- solved in 50 c.c. 10 per cent ci- trate.	20.69	Stood ten minutes be- fore titrating.
6.	0.750 grm. (25 c.c.) solid salt dissolved in 50 c.c. 10 per cent citrate.		21.10	Stood ten minutes be- fore titrating.

Nos. 3 and 5 show that if sufficient time is given to allow equilibrium to be established, the results are practically the same whether the 50 c.c. solution is evaporated to dryness and dissolved in 50 c.c. of 10 per cent citrate (20.69 c.c.), or 25 c.c. of solution are treated with 25 c.c. of 20 per cent citrate, and the solution allowed to stand sixteen hours (20.62 c.c.). No. 6 in this series, as well as No. 7 in Series B, shows that the same result is not reached when dissolving the solid

salt in citrate (B 7 = 21.90) and titrating as when evaporating to dryness, and re-dissolving in the same amount of citrate (B 6 = 21.62). Commercial alum is evidently not a homogeneous body, and further combination between the alumina or basic sulphate and the sulphuric acid takes place after solution in water.

The analytical method as finally worked out is as follows:—Dissolve 3 grms. of alum in 100 c.c. of water. Take 25 c.c. sample, add 50 c.c. strictly neutral 10 per cent potassium-sodium tartrate, and titrate with fifth-normal barium hydroxide, using phenolphthalein as indicator. This is equivalent to the sulphuric acid combined with the alumina plus the free acid. Evaporate a duplicate 25 c.c. sample to dryness on the water-bath, dissolve in 50 c.c. strictly neutral 10 per cent sodium citrate, allow to stand ten minutes, and titrate with barium hydroxide, with phenolphthalein indicator as before. The difference between these results is equivalent to one-third of the sulphuric acid combined with the alumina, and hence to one-third of the alumina. The barium hydroxide solution should be standardised by a blank determination upon a solution of sulphuric acid in which approximately enough precipitated aluminum hydroxide has been dissolved to correspond to aluminum sulphate. The aluminum hydroxide may be best made by precipitation of the chloride to ensure absence of sulphate. Caustic soda, even when freed from carbon dioxide by barium hydroxide, does not give such satisfactory results as the barium hydroxide. As examples of the practicability of the method the following results on two widely differing alums are cited:—

Alum B, a C.P. Aluminum Sulphate.

30 grms. per litre (25 c.c.) sample = 0.750 gm. sample.

	C.c.
Fifth-normal barium hydroxide for tartrate titration	32.50
Fifth-normal barium hydroxide for citrate titration	32.55
	21.60
	21.63
Difference	10.90

$10.90 \times 3 = 32.70$ c.c. fifth-normal barium hydroxide equals total sulphur trioxide theoretically necessary to combine with alumina, and therefore equals alumina.

$32.70 \times 0.003407 = 0.1114$ gm. alumina equals 14.86 per cent alumina. Alumina determined gravimetrically equals 14.73 and 14.80.

The close agreement between the figures 32.52 c.c. (free and combined sulphur trioxide) and 32.70 c.c. (combined sulphur trioxide) show that the alum is almost exactly neutral with an excess equal to 0.18 c.c. of fifth-normal alumina.

Alum C, a Commercial Aluminum Sulphate.

30 grms. per litre (25 c.c.) sample = 0.750 gm. sample.

	C.c.
Fifth-normal barium hydroxide for tartrate titration	33.59
Fifth-normal barium hydroxide for citrate titration	33.59
	20.64
	20.74
Difference	12.90

$12.90 \times 3 = 38.70$ c.c. fifth-normal barium hydroxide equals total sulphur trioxide theoretically necessary to combine with alumina, and therefore equals alumina.

$38.70 \times 0.003407 = 0.1318$ gm. alumina equals 17.58 per cent alumina. Alumina determined gravimetrically equals 17.57 and 17.50.

$38.70 - 33.59 = 5.11$ c.c. fifth normal alumina equals 0.0174 gm. alumina equals 2.32 per cent alumina more than is sufficient to form aluminum sulphate.

Alum B, as shown by the above figures, is slightly basic, but a determination of free acid by the method of

Beilstein and Grosset gave 0.9 per cent free acid (*Bulletin de l'Académie Imperiale des Sciences in St. Petersburg*, 1890, p. 147). This method of Beilstein and Grosset has been investigated by V. Keler and Lunge (*Zeit. Angew. Chem.*, 1894, p. 669), who state that it gives results which are uniformly slightly high but otherwise very accurate, and it therefore became necessary to explain the discrepancy. The method of Beilstein and Grosset is as follows:—Dissolve 1 or 2 grms. of alum in 5 c.c. of cold water, add 5 c.c. of a cold saturated solution of ammonium sulphate, allow to stand, with frequent stirring, for fifteen minutes, and then add 50 c.c. 95 per cent alcohol. Filter, wash with 50 c.c. 95 per cent alcohol, evaporate to dryness on water-bath, dissolve in water, and titrate with tenth-normal potassium hydroxide, using litmus as indicator. All the alum is, in this process, supposed to be precipitated as normal ammonium alum together with most of the excess ammonium sulphate, and the free sulphuric acid remains in solution together with a small amount of ammonium sulphate. Three determinations of free acid in alum B by this method gave 0.86, 0.88, and 0.89 per cent free acid as sulphur trioxide—as good an agreement as could be desired. To test whether an error in Beilstein and Grosset's method due to hydrolysis might not be responsible for this apparent free acid, variations were made in amount of water and concentration of sulphur trioxide with the following results:—

Sample Grms.	Water. C.c.	Saturated solution (NH ₄) ₂ SO ₄ . C.c.	Alcohol. Per cent.	Free acid as SO ₃ . Per cent.
2	10	10	95	0.96
3	10	10	95	0.88
3	5	10	absolute	0.70
3	5	5+5 grm. solid ammonium sulphate.	absolute	0.61

Blank determinations showed that the change in results was not due to impurities in the ammonium sulphate or alcohol. The results show that the decrease in the relative amount of water decreases the apparent amount free acid, but although hydrolysis does thus play a part in influencing the results, there remains as the lowest figure, 0.6 per cent, which can hardly be attributed to an error in the method. Turning back to the series of results obtained by titrating alum B in presence of citrate, it was remarked that the figures obtained by dissolving the alum directly in citrate were higher than those obtained by dissolving the alum in water, then evaporating to dryness, and re-dissolving in citrate which showed a greater amount of free acid in the original alum than after evaporation to dryness. If the results in B 7 are taken and calculation made we find that there are required:—

Fifth-normal barium hydroxide for tartrate titration	C.c.
Fifth-normal barium hydroxide for citrate titration when alum dissolved directly in citrate	32.52
Difference	21.90
10.62 × 3 = 31.86 c.c.	10.62
32.52 - 31.86 = 0.66 c.c. = 0.70 per cent free acid as sulphur trioxide.	

This result is in fair accord with the results obtained by the Beilstein and Grosset method of direct estimation, and probably corresponds closely to the amount of free acid actually present in the solid salt. It is entirely incorrect, however, to hold that the solution of this alum will have that amount of free acid, as the results already given show that the amount of alumina in solution is slightly greater than the amount necessary to form the normal salt. The solid salt is evidently not uniform. When dissolved in water to dilute solution, these inequalities disappear quickly. In concentrated solution, as in the Beilstein and Grosset method, or when the salt is dissolved in citrate, equilibrium is attained much more slowly, and a titration

of such a solution soon after solution is complete gives approximately the conditions prevailing in the solid salt. If the solution is allowed to stand a sufficient length of time, equilibrium is finally reached, as shown by experiments C 3 and C 5 (*ante*).

Summary.

If a solution of an alum to which has been added neutral potassium sodium tartrate (Rochelle salt) is titrated with barium hydroxide, the barium hydroxide used will correspond to the sulphuric acid combined with the alumina plus the free acid. The sulphuric acid combined with sodium or potassium is not estimated. If a duplicate solution of alum is evaporated to dryness, re-dissolved in neutral sodium citrate, and titrated with barium hydroxide, a smaller quantity of barium hydroxide is required, and the difference between the amounts of barium hydroxide used in the two titrations is equivalent to one-third of the alumina. From these two titrations can be calculated the alumina and the sulphuric acid combined with it, whether the alum be basic or acid, and if the alum is acid, the excess of acid over that necessary to form the normal sulphate. Commercial aluminum sulphate may, in its solid state, carry free acid, although in the solution such uncombined acid may disappear, combining with what had been basic portions of the solid salt. Such free acid may be estimated by dissolving the solid salt directly in citrate, and titrating with barium hydroxide at once. This method gives results closely concordant with Beilstein and Grosset's method, but it does not show that the alum contains more acid than is sufficient to form with the alumina the normal salt.

When aluminum sulphate is titrated with barium hydroxide thus, in presence of neutral alkali tartrate or citrate, the precipitation of barium sulphate is retarded for a time, varying from a few minutes to several hours, and when the precipitate does form it is in a very peculiar colloidal form which is undergoing further investigation. Consideration of this subject, and also of the action of salts of other metals than aluminum and salts of other acids than tartaric and citric, as well as the theoretical points involved, are reserved for a following paper.

MISCELLANEOUS.

Mixtures of Sulphur and Phosphorus formed below 100°.—R. Boulough.—There does not appear to exist any phosphorus sulphide having a definite composition which is formed at a temperature below 100°. However, there are found mixed crystals of sulphur and phosphorus rich in sulphur and isomorphous with octahedral sulphur, which can easily exist in the liquid state in false equilibrium. Besides these, crystals rich in phosphorus can be obtained isomorphous with this body, and which can be isolated even at a very low temperature, owing to the same false equilibrium. A further crystal conglomerated of the two species of mixed crystals containing 0.228 of sulphur to 0.772 of phosphorus, and which melts suddenly and completely at 9.8°, also exists, and may easily be confused with a definite compound.—*Comptes Rendus*, cxxxv., No. 3.

ERRATUM.—P. 87, line 1, col. 1 of Table, for "1 Hg" read "1 H."

NORTHERN POLYTECHNIC INSTITUTE, HOLLOWAY, LONDON, N.

The Governors of the above Institute invite applications for the Post of HEAD of CHEMICAL DEPARTMENT. Salary £250 per annum for whole time service. Duties to commence on Sept. 18th, or as soon after as possible. Applications to be sent in by Sept. 3rd on special forms to be obtained from—

August 12, 1902. W. M. MACBETH,
Clerk to Governors.

SILICIOUS FLUOR NATRUM (KIESELFLUORNATRIUM).

Pure white and beautifully dry article to be disposed of. Annual production, 80,000 to 100,000 kilograms. Address, "K. H. 1740," care of Rudolf Mosse, Cologne.

THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2232.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; one commencing on September 15th, one on the second Monday in January, and the third on the second Monday in June (or July, as may hereafter be determined).

The Regulations for Matriculation have recently undergone revision, but an Examination under the old Regulations will be held in January, 1903, and (in addition to that under the revised Regulations) in June, 1903, but not thereafter.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations (except that in September) may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must apply to the Principal for a Form of Entry, which must be returned within a specified time before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Principal, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English; one paper of three hours. (2) Elementary Mathematics; two papers of three hours each. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany; one paper of three hours in each subject. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3); one paper of three hours in each subject; if Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern:—Latin, Greek, French, German, *Arabic, *Sanskrit, *Spanish, *Portuguese, *Italian, *Hebrew, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary, Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, Elementary Biology

—Botany, *Elementary Biology—Zoology. Candidates for Examination in subjects marked with an asterisk must give at least two months' notice; there will be no Examination in them in September, 1902.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry two papers will be set and a practical examination.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with the Form of Entry he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis,

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.
Lees Reader in Chemistry—A. Vernon Harcourt, F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, J. Watts, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Emmanuel, Sidney, Pembroke, Caius, and Downing Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Assistant Lecturer—Emil A. Werner, F.C.S., F.I.C.

Demonstrators—W. Haughton, M.B., and W. C. Ramsden.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 2nd of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced, including Physical Chemistry, second year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Freshmen, and tenable for five years. These Foundation Scholars receive £20 per annum, have free commons, their chambers for half the charge paid by other students, and their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(DIVISION OF ENGINEERING, ARCHITECTURE, AND APPLIED SCIENCE).

Professor of Chemistry—J. M. Thomson, F.R.S., F.C.S.
Lecturer—Herbert Jackson, F.C.S.

Demonstrators—P. H. Kirkaldy, F.C.S., and D. Northall Laurie.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1902-1903 are October 2, January 15, and April 23.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit

their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s.; per ann., £8 8s.; Practical Chemistry per term, £4 4s.; per ann., £10 10s.; Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; Three months, £10 10s.; Six months, £18 18s.; Nine months, £26 5s. Three days a week: One month, £2 12s. 6d.; Three mos., £6 6s.; Six mos., £11 11s.; Nine mos., £15 15s.

METALLURGY.

Professor—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, F.R.S., F.C.S.

In addition to the regular College Course in Photography occasional classes may be formed. For further particulars application should be made to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professors—Sir William Ramsay, LL.D., F.R.S., &c. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—Morris Travers, D.Sc.; E. C. C. Baly, F.I.C.; and F. G. Donnan, M.A., Ph.D.

The Session is divided into three Terms, as follows:—First Term, from Thursday, October 2nd, till Friday, December 19th; Second Term, from Tuesday, January 13th, till Friday, March 27th; Third Term, from Tuesday, April 21st, till Saturday, June 13th. Class Examinations begin on June 15th.

Junior Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Saturday, 11 to 1. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Senior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

In this Course the physical principles bearing on Chemistry, are first discussed, and the Chemistry of the Elements and their compounds are treated in considerable detail, under the headings—Elements; halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 o'clock, on the chief types of Carbon Compounds.

An Exercise Class will meet once a week throughout the Session.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning in January. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent researches bearing on Chemical Theory.

Third Term: Some Lectures will also be given on Saturdays at 9, during the Third Term, on the History of Chemistry.

Organic Chemistry.

Mondays, Wednesdays, and Fridays, at 9, during the session.

This Course will consist of three lectures a week during the whole Session, and is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the preceding Course, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

An Advanced Course will be held twice a week during the second and third terms, for those engaged in prosecuting research in Organic Chemistry. Fee, £2 12s. 6d.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Demonstrators—H. Chapman Jones and M. O. Forster, Ph.D., B.Sc.

Assistants—G. S. Newth, J. C. Philip, M.A., Ph.D., B.Sc., and H. Burrows, Ph.D.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Board of Education. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship

of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science. The Associateship of the Royal College of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, and Geology, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction lasts for three years, is the same for all the divisions during the first year, after which it is specialised according to the particular division in which the student is working for the Associateship.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first year, and, in the second and third year, those subjects prescribed as necessary for the division in which he seeks to obtain his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the necessary examinations receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Astronomical Physics	2	3
Mine Surveying	10	

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to £40.

The Session is divided into two Terms. The first Term begins about the first week of October, and ends about the middle of February. The second Term begins in the middle of February, and ends about the middle of June.

The hours of study are from 10 a.m. to 1.15, and from 2 to 4 p.m. every day, except on Wednesday and Saturday, when the College closes at 1 p.m.; students receiving instruction in Mathematics and Mining attend till 5 p.m. on specified days.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a sum not exceeding £3 towards their expenses.

THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-first Session will commence on Oct. 1, 1902. **Professors**—Chemistry, W. Palmer Wynne, D.Sc., F.R.S., F.I.C.; Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Demonstrators—H. Hibbert, M.Sc. (Vic.), and A. Brooke, Ph.D. (Strassburg).

Lecturer in Agricultural Chemistry—J. Alan Murray, B.Sc. (Edin.).

Lecturer on Dyeing—E. J. Wilkinson.

The College is open to male and female students above the age of sixteen years. The Session commences on October 1st, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly throughout the Session. (2) Intermediate Science Course; four lectures weekly throughout the Session. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1902-1903, Course A). (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the

College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 18, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Alexander Lauder, B.Sc., F.C.S. Assistant Lecturer in Agricultural Chemistry, Alan Baguley, B.Sc. Scholar Assistant, C. K. Tinkler.

Physics.—Professor, E. Taylor Jones, D.Sc.

The Session opens October 1st, 1902. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Session £3 3s.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrators—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 26th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Inorganic Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Lecturer—Francis E. Francis, M.Sc., Ph.D.

Demonstrator—Oliver C. M. Davis.

The session 1902-1903 will begin on October 7. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of

Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar and Secretary.

DAY LECTURES. *Inorganic Chemistry.*

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Elementary Course.—Two Lectures a week will be given during the Session. Fee, £4 4s.

Special Course.—A special course of Lectures is also given to Engineering Students.

Intermediate Course.—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Elementary and Intermediate Courses.

Advanced Course (Parts I. and II.).—One Lecture a week in each part will be given throughout the Session. Fee for each course, £2 12s. 6d.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given throughout the Session. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, Metallurgy, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

Pharmaceutics.—During the second and third Terms a course of Lectures will be given one evening a week dealing chiefly with the *Materia Medica*, Pharmacy, and Chemistry of the British Pharmacopoeia. Fee, £1 1s.

Practical Chemistry.—Laboratory Instruction.—The Laboratory will be open two evenings a week from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar and Secretary.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY AND METALLURGY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—G. P. Darnell-Smith, B.Sc., F.I.C., F.C.S.;

H. A. M. Borland, A.R.C.S.; A. J. Carrier, B.Sc.

Demonstrators—F. B. Gatehouse; H. C. Shilstone; H. R. Tutton.

Assistant in Chemical Laboratory—C. E. Young.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry, Analysis, and Assaying, to Students of either sex. They include the Junior Laboratory (for forty Students working at one time), Senior Laboratory, Gas Analysis Room, Balance Room, Combustion Room, Store Rooms, and Metallurgical Laboratory. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture, and to train them in practical Metallurgical processes, especially Assaying.

Special facilities will be given to Students wishing to undertake research work approved by the Principal; and the Courses provide completely for the Preliminary Scientific Examination (M.B.), and for the Examinations in Chemistry for the B.Sc. degree of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute, provided the details in each case be certified by the Professors.

Certificates of Proficiency in Assaying will be given to Students who complete a Course of not less than two years' work in the Metallurgical Department, and pass satisfactorily the College examinations in the Theory and Practice of Assaying.

The Laboratories are open every week-day from 9 till 12 noon, and from 1.30 to 4.30 p.m., except Saturday, when they close at noon.

The Annual Fee of £10 10s. secures (in addition to the use of either or both Laboratories) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and the Engineering Workshop.

The College Evening Classes, available to persons of either sex, will commence on Monday, September 29th.

Further detailed information may be obtained from the College Prospectus, price 6d.

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S.

Assistant Lecturers and Demonstrators—T. S. Price, Ph.D., D.Sc.; Alex. Findlay, M.A., D.Sc., Ph.D.; Alex. McKenzie, M.A., D.Sc., Ph.D.

The Session will be opened on October 1st, 1902.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. At least one of the above meetings of the class in each week will be devoted to tutorial work. Attendance at this tutorial class is compulsory, as is the performance of the weekly exercises set by the Professor. Mondays to Fridays inclusive, at 9.30 to 10.30 a.m. Fee, £5 5s. B. This part of the course in-

cludes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—*Advanced Organic Chemistry.*—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with various Chemical subjects. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General, Physical, and Organic Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in September.

Bowen Scholarship.—One Open Scholarship in Metallurgy of the value of about £96 is awarded annually in September.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

BRADFORD MUNICIPAL TECHNICAL COLLEGE.

DEPARTMENT OF CHEMISTRY AND DYEING.

Head of Department—W. M. Gardner.

Lecturers in Chemistry—B. North, A.R.C.Sc. (Lond.); S. F. Stell, F.C.S.; and W. Trotter.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Lecturer in Metallurgy—W. J. Willis.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer on Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over three years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Chemical Philosophy, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over three years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Extending over one or two years.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on three half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

VIII. Attendance at the College Courses and College Certificates in Chemistry, Physics, Animal Biology, and Botany are recognised by the Conjoint Board for Medical Studies.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Lecturer in Organic Chemistry—Julius B. Cohen, Ph.D.

Assistant Lecturers and Demonstrators—T. S. Patterson, Ph.D.; J. McCrae, Ph.D., and H. M. Dawson, B.Sc., Ph.D.

Demonstrator—C. E. Whiteley, B.Sc.

The Session begins October, 1902.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.
2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.
3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.
4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses—

- (a) Organic Chemistry.—Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.
 (b) History of Chemistry.—Monday and Wednesday at 9.30 a.m. in the First Term. Fee, £1 1s.
 (c) Physical Chemistry.—Thursday and Saturday at 9.30 a.m. in the Second and Third Terms. Fee, £2 2s.
 (d) Selected subjects.—Tuesday at 9.30 a.m. in the Second and Third Terms. Fee, £1 1s.
 (e) Electro-chemistry.—One hour weekly. 3rs. 6d.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 p.m., from January to March. Fee, £5 5s.

Elementary Science for Teachers.—Saturdays, 9.30 to 12.30, for half the session. £2 12s. 6d.

Dyeing Department.

Professor—J. J. Hummel, F.I.C.

Lecturer and Research Assistant—A. G. Perkin, F.R.S.E.

Assistant Lecturer—A. B. Steven, B.Sc.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Leather Industries Department.

Professor—H. R. Procter, F.I.C.

Assistant Lecturer and Demonstrator—Andrew Turnbull, Ph.D.

Demonstrator—F. Austyn Blockey.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—H. Ingle, F.I.C.

The full Course occupies two years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the Yorkshire College.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor—J. Campbell Brown, D.Sc.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—T. L. Bailey, Ph.D.

Demonstrators and Assistant Lecturers—T. L. Bailey, Ph.D.; A. T. de Moulpied, B.Sc., Ph.D.; and A. W. Titherley, D.Sc., Ph.D.

Assistant—H. H. Froyell.

The Session commences October 2nd.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for the Pharmaceutical Diplomas; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4.

Pharmacy Courses: Junior, £3; Senior, £3.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3.

Course B.—Metals. Fee, £3.

Course C.—Organic Chemistry. Fee, £3.

Course H.—Special Organic Subjects. Fee, £2.

Course D.—Physical Chemistry, with Practical Work. Fee, £2.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, and Gold, and other Metals. (5) Distillation of Coal and Tar Industries. (6) Fuel and Gas. (7) Chemistry Applied to Sanitation. (8) Technical Gas Analysis. (9) Electrochemical work. Three terms. Fee, each course £1 10s.

Practical Classes.

(1) Preliminary. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances; preparation of Inorganic Compounds. (3) Revision Class. (4) Senior: Practical Organic. (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Examination of Water and Air, &c. (6) Quantitative Class.

Chemical Laboratory.

The Chemical Laboratories recently erected provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water Analysis, Gas Analysis, Photometry and Photography, Electro-chemical Work, Metallurgy Laboratories, and a Research Laboratory. New stores for students' apparatus and chemicals have also been built and placed in charge of a skilled dealer.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided.

TABLE OF FEES.

Per Week.	One Term, Three Months.	Three Terms, One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

Pharmaceutical Course (see special syllabus).

Technological Curriculum.

Preliminary Year.—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics,

Elementary Engineering, Drawing, and Design (in this or one of the following years). German. Or, the Victoria Preliminary Course and Examination may be taken.

First Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

Second Year.—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course D or E, Technological Chemistry, Course F. Chemical Laboratory, four days per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

Third Year.—In the third year the student should begin to specialise. The following are possible alternatives:—1. Courses D, E, and F; Course H. Any other Courses omitted in a previous year. Laboratory, five days per week. The Degree of B.Sc. in the Honours School of Chemistry may be taken. 2. Metallurgical Classes. Metallurgical Laboratory, two days per week. Chemical Laboratory, Gas Analysis, and Electro-chemistry, two days per week. Physical and Electrotechnical Laboratory, one day per week. 3. Courses D, E, and F. Physics (Senior Course). Chemical Laboratory, four days per week. Physical Laboratory, one day per week. 4. Courses D and F, and a course on Chemistry applied to manufacturing operations. Chemical Laboratory, three or four days per week. Engineering Laboratory and Electrotechnical Laboratory, one day per week.

Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry may be taken after 1, 2, or 3. Those who have taken the Ordinary Degree of B.Sc. may pass the Victoria M.Sc. Examination in any subsequent year.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1902, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15, 1902. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes, including laboratory work, will be held during the winter.

The Prospectus containing full particulars may be obtained from the Secretary, University College, Liverpool.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturer in Chemistry—F. C. Garrett, M.Sc., F.C.S.

Lecturer in Agricultural Chemistry—S. Hoare Collins, F.I.C., F.C.S.

Assistant Lecturers and Demonstrators—J. A. Smythe, M.Sc., Ph.D., and H. W. Cousins, B.Sc.

First Year Courses.—1. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will

commence on Wednesday, October 8th. Fee, £3 10s. for the Session.

II. *Special Course.*—More advanced than the above. Mondays and Fridays, 11 to 12. Fee, £3 10s. for Session.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 7th. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s. Also special class in Crystallography.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m.

Metallurgy and Assaying.—Lecturer, Professor Louis, M.A., F.I.C., F.C.S.; Demonstrator, G. H. Stanley, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the three following examinations:—

1. The first examination for the Degree of B.Litt.
2. Durham Examination for certificate of proficiency in General Education, held in March and September.
3. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Science.—Every candidate for the Associateship in Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the second year in an examination in a more advanced stage in any two of these subjects. Associates in Science are admissible one year after obtaining the title of Associate to the examination for the degree of Bachelor of Science of the University of Durham.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 29th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry—W. H. Perkin, Ph.D., F.R.S.

Demonstrators and Assistant Lecturers—George H. Bailey, D.Sc., Ph.D.; W. A. Bone, D.Sc.; P. J. Hartog, B.Sc.; D. L. Chapman, B.A.; Norman Smith, B.Sc.; and F. V. Darbishire, B.A., Ph.D.

Demonstrator in Organic Chemistry—F. A. Lidbury, B.Sc.

Lecturer in Technical Organic Chemistry—Jocelyn F. Thorpe, Ph.D.

Professor and Director of the Physical Laboratories—Arthur Schuster, Ph.D., F.R.S.

Assistant Lecturer in Metallurgy—Dr. Bone.

The Session begins on October 7, 1902.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Tuesdays, Thursdays, Saturdays, 11.30 a.m., during the two Winter Terms. The Metals.

Third Year Honours Course.—At times to be arranged. Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, 9.30, during two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Thursdays, 9.30, during the two Winter Terms.

History of Chemistry and Chemical Philosophy.—Wednesdays, 9.30, during the Session.

METALLURGY.—*Lectures:* The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical:* The Metallurgical Laboratory will be open to students every day.

ELECTRO-CHEMISTRY.—In connection with the new John Hopkinson Memorial Laboratory, rooms have been fitted for the study of Electricity in its applications to Chemistry. Courses of lectures and laboratory instruction will be given to Advanced Chemical Students in the coming Session. *Lecturer*—R. S. Hutton, B.Sc.

The Chemical Laboratories are open daily from 9.30 a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

Courses for B.Sc. Degree.—To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours

Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £100 is awarded annually among the Graduates in Science for the encouragement of Research. Among the College Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; &c.

Applied Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

ELECTRO-CHEMICAL LABORATORY.

In the new Laboratories there is a complete equipment for Electro-chemical and Electro-metallurgical work. *Demonstrator and Assistant Lecturer in Electro-technics*, Robert Beattie, B.Sc. (Durham). *Demonstrator and Assistant Lecturer in Electro-chemistry*, R. S. Hutton, M.Sc. (Vict.). *Assistant Demonstrators*, James Lord, B.Sc. (Vict.); R. C. Wale, B.Sc. (Vict.).

For further particulars apply to the Registrar, Mr. S. Chaffers.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. D. Lander, D.Sc.; and G. Sand, Ph.D., M.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on October 6th, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses

on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on Electrochemistry and other special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations. Special lectures will also be given in Pharmacy, Materia Medica, and all other Pharmaceutical subjects.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

UNIVERSITY COLLEGE, SHEFFIELD.

Professor of Chemistry—W. Carleton Williams, B.Sc., F.C.S.

Lecturer—G. Young, Ph.D., F.R.S.E.

The Session will commence on October 1st.

Matriculation Course.—Tuesday and Friday 10 to 11. Fee, £2 2s.

Intermediate Course.—Inorganic Chemistry. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

Organic Chemistry.—Elementary: Saturdays, 10 to 11; fee, £1 11s. 6d. Honours: Tuesdays and Thursdays, 12 to 1; fee, £2 12s. 6d. Advanced: Thursdays, 4 to 5; fee, £1 11s. 6d. Special Course: Hours to be arranged; £1 11s.

Physical Chemistry.—Tuesday, 11 to 12. Fee, £1 11s. 6d.

Chemical Philosophy.—Thursday, 11 to 12. Fee, £1 11s. 6d.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health and for the Licentiate of Sanitary Science, will be held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9. Sessional Fee, Lecture Class and Laboratory, on Wednesday evening, £1 10s. Fee for one term, 17s. 6d.

DEPARTMENT OF METALLURGY.

Professor of Metallurgy—J. O. Arnold. This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a new laboratory for the study of the micrographic analysis of metals has been completed and fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students engaged in Collieries or Gas-Works.

A new steel works is now being erected in connection with the Sheffield College at a cost of about £10,000. The works are designed to include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works will also be provided with a hammer and rolling mill capable of dealing with four-inch ingots. Differential annealing furnaces, oil-brightening and lead-tempering tanks will constitute part of the new plant. Additional laboratory accommodation will be attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—James Walker, Ph.D., D.Sc., F.R.S.

Assistant Lecturers—J. S. Lumsden, Ph.D., D.Sc., and J. K. Wood, D.Sc.

Lecture Assistant and Laboratory Steward—J. Foggie, F.C.S.

The Winter Session begins on October 14th, and ends on March 18th. The Summer Session extends from the middle of April to the end of June.

The *Junior Lecture Course on Systematic Chemistry* is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—W. B. Davidson, M.A., D.Sc., and F. W. Gray, M.A., B.Sc.

I. *General Lecture Course (100 Lectures)*.—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £3 3s.; for subsequent attendance, £2 2s. A Tutorial Class (without fee), conducted by the Senior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry (50 Lectures)*.—Daily during the Summer Session. Fee, £2 2s.

III. *Practical Course for Medical Students*.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

IV. *Chemical Laboratory*.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

In connection with the Laboratory work, three Lectures a week on Physical Chemistry and selected portions of Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. W. B. Davidson. Fee, £2 2s.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

This course is given during the Winter Session, and includes both Lectures and Laboratory work. The Lectures deal with the chemistry of the atmosphere, the soil, manures, and foods. The physiological chemistry of plants and animals, the composition and manurial requirements of crops, and dairy chemistry, are also treated of. The Laboratory work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of soils, manures, feeding stuffs and waters, and with the impurities and adulterations of these, occupy much of the time given to practical work. The fee for the whole course—lectures and practical work—is £3 3s.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—Alex. Crum Brown, M.D., D.Sc., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from middle of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session; fee, £2 2s. An Intermediate Course is held in summer; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin; fee £1 rs.; and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

Laboratories.—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry, including Gas Analysis, Metallurgy, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a

choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; and J. P. Longstaff, B.Sc.

The Session begins September 29th, 1902.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the third year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

Matriculation Fee, 5s.; Composition Fee for Engineering Courses, £10 10s.; for Chemistry Courses, £10 10s., £12 12s., £15 15s. Full particulars are published in the Calendar of the College early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1902-1903 may be had from Mr. H. F. Stockdale, the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry—T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 14th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about forty-three Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 26th and following days. Twenty-six of these Bursaries are restricted to Men, three to Men or Women, and about fourteen to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Examinations, so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Second B.Sc. Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—

(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for each course of Practical Chemistry is £3 3s. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—Chemistry.—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—

(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry*.—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils*.—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four consecutive years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—Robert Elliott Doran, F.C.S.

The College Session will commence on October 21st, 1902, and end on June 13th, 1903. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be specially arranged as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1903.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics,

First-class value £42, and Second-class value £21, together with other prizes, e.g., a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time also been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senior, Ph.D., M.D., F.I.C., F.C.S.

Demonstrator—William Goodwin, F.C.S.

The College Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer a Scholarship of £150 per annum. This Scholarship has just been awarded for the third time to a Chemistry Student of this College, and to another Student it has been renewed for a third year.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Professor of Chemistry—W. N. Hartley, F.R.S.

Assistant Chemist—J. Holms Pollok, B.Sc.

Demonstrator of Chemistry and Assaying—A. E. B. Manders.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering, and Manufactures, Physics, and Natural Science. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Organic

Chemistry; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

The following are supplementary courses of instruction:—

- (1) Laboratory Instruction in the Theory of Chemistry.
- (2) An Analytical Course for Students in Engineering.
- (3) A Course of Practical Chemistry for Medical Students.
- (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health.
- (5) A Course of Chemistry for Pharmaceutical Students.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitors, who have been a year in the College.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 6d., net.—*City and Guilds Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 23rd, and the Winter Session opens on Tuesday, October 7th. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: 1. Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science

and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 23rd. Session begins October 7th. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. H. W. Harrie, F.C.S., and C. A. West, B.Sc., &c. Session commences Sept. 29.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells, Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), assisted by Mr. John L. White, M.Sc., Mr. H. G. Wayling, B.Sc., and Mr. B. C. Polkinghorne, B.Sc., F.C.S. Day and Evening Classes in Science and Art subjects. Session opens Sept. 16. The principal work of the Institute is the provision of Evening Classes for both sexes in all subjects of Technology, Pure and Applied Science, Art, Commerce, Domestic Economy, and Music; but it also provides a Technical Day School, a Science Day School for Boys and Girls, a Training School of Domestic Economy, a Domestic Economy School for Girls, a Day School of Art, and Special Day Courses in Science and Technical subjects. During the last Session, 250 Evening Classes in more than 100 different subjects were attended by over 3100 individual students, while 520 students were in regular attendance at the Day Schools and Classes.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, Breams Buildings, Chancery Lane.—Chemistry Courses will be conducted, commencing Monday, September 29, adapted for the Elementary, Advanced, and Honours Examinations of the Board of Education and for various Examinations for the B.Sc. and M.E. Degrees of the London University, by Mr. J. E. Mackenzie, Ph.D., D.Sc. This Institution, which has now completed seventy-nine years of educational work in the metropolis, commences its new Session on Monday, September 29th. The Day and Evening courses of study, comprise the various branches of Natural Science, Mathematics, classical and modern Languages, Economics, Commercial Subjects, Law, Mental Science, Music, and Art. The courses provide for the Examinations of the University of London, in the faculties of Arts, Science, and Commerce, those of the Conjoint Board, Civil Service, &c. The Report for the last session shows that during the year 58 students passed some university examination, while large numbers gained successes at various public examinations. The Institution has had many additions to its appliances in recent years, and the Physical, Chemical, Biological, and Metallurgical laboratories are now very thoroughly equipped. The Day classes provide courses in Chemistry, Biology, Physics, Mathematics, and Geology for the Science Degrees of London University. There are also Day classes in modern Languages, including Russian and Spanish; courses of Lectures on French and German Literature are given both in the afternoon and evening. The School of Art is open both day and evening. A new reading room, and a new magazine room have recently been provided. The Metallurgical laboratory has been extended and reorganised, and classes are held both in the day and evening. The Calendar supplies complete syllabuses of the classes and full information about the Institution. A Lecture or Entertainment is given in the Theatre every Wednesday evening.

BRIXTON SCHOOL OF CHEMISTRY AND PHARMACY, 171, Brixton Road, London.—Principal, Dr. A. B. Griffiths, F.R.S. (Ed.). Lectures on Inorganic and Organic Chemistry, Physics, Botany, &c., for Pharmaceutical, Medical, and other students. The benches in the laboratory are fitted with every convenience. There are courses in Research Work. Full particulars as to fees, &c., may be obtained by writing to the Principal.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road (near the Obelisk).—Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 5s. to 20s.). Day Practical class in Electro-chemistry, lecture on Friday evenings (70s.) Special Saturday Morning Class in Practical Chemistry (10s.); Dr. F. Mollwo Perkin, assisted by Dr. E. C. Jee and A. Fontana, B.A. Electricity and Magnetism: Evening Lectures and Laboratory Work (Session fees, per course, 8s. to 10s.), Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painter's Oils, Colours, and Varnishes. Session opens Monday, September 22, 1902.

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Herbert Tomlinson, B.A., F.R.S. Professor of Chemistry, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry, including Metallurgy, Assaying, &c. Special Classes are held for the Matriculation, Intermediate Science, and B.Sc. Examinations of the University of London. Prospectuses of Day and Evening Classes may be obtained from the Secretary, 1d. each, by post 2½d.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemistry Department, Arthur Lapworth, D.Sc.(Lond.), F.I.C.; Assistants, Mr. A. C. O. Hann and others. Lectures and Practical Classes in General Chemistry and Photography, also in Chemistry applied to other industries, are held in the evenings from 7.15 to 10, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties. Session commences September 22.

EAST LONDON TECHNICAL COLLEGE, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistant Lecturer and Demonstrator, F. G. Pope. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination (B.Sc). Evening Classes are also held. The Day College opens on Sept. 8. Evening Classes begin Sept. 23.

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Head of Chemical Department, Mr. H. Charles L. Bloxam. Assistants, Mr. W. H. Watson, A.R.C.S., Mr. F. E. Grant, B.Sc. Lectures and Practical Classes in Elementary, Advanced, and Honours Inorganic and Organic Chemistry are held in the evenings from 6.30 or 7 p.m. to 9.30 p.m., affording instruction in the Courses for the Examinations of the University of London and the Board of Education. The Classes form a Course of Study extending over five Sessions, and are open to both sexes. The Laboratories are open to those wishing to pursue investigations. A reference library is attached to the Chemical Department. Session begins September 22.

NORTHAMPTON INSTITUTE (City Polytechnic), St. John Street Road, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Lecturers in Technical Chemistry: Mr. S. Field, A.R.C.S., and Mr. G. Naylor. Day and Evening Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping and Stereotyping. (For full details see Prospectus).

CARPENTERS' COMPANY TECHNICAL INSTITUTE, Jupp Road, Stratford, E.—Principal, William Ping, F.C.S. Evening Classes in Theoretical and Practical Chemistry, and in many other Departments of Science and Art. Day Technical School.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

IMPERIAL COLLEGE OF CHEMISTRY AND PHARMACY, 49 and 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *re* the Institute of Chemistry Examination. Students attending the College visit technical works.

WEST HAM MUNICIPAL INSTITUTE.—Principal, Albert E. Briscoe, B.Sc. (Lond.), &c. Chemical Department, Harold A. Auden, M.Sc., &c., assisted by F. H. Streatfeild and H. V. Capsey. Day and Evening Classes.

SOUTH-EASTERN AGRICULTURAL COLLEGE, Wye, Kent.—Chemistry: Lecturer, E. J. Russell, D.Sc. (Lond.); Demonstrators, F. J. Holbrook and F. J. Flymen. Session begins October 1. The courses of instruction in Chemistry are suitable to students intending to become analysts or assistants in works manufacturing manures, feeding-stuffs, &c. The College possesses new and well-equipped Laboratories for Chemistry, Botany, and Bacteriology. The farm, gardens, and experiment grounds afford material for investigation and research. Fee: £8 6s. 8d. per term admits to all Lecture Courses, &c.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc.(Lond.), &c., assisted by Mr. W. H. Duckworth and Mr. Jos. Yates. Session opens Monday, September 15. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 2½d.).

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, J. Paul de Castro, M.A. (Cantab.), A.I.C., F.C.S., assisted by a staff of Mining Engineers and Mine Surveyors. Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, and Blow-pipe Analysis, for intending Assayers and Mineral Chemists. Shorter Courses are also held in the above subjects to meet the requirements of intending Mining Engineers, and Prospectors. Practical instruction in Mining given at Pednandrea, the School Mine. Syllabus on application to the Registrar. Session commences Wednesday, September 10.

INSTITUTE OF PUBLIC HEALTH AND TECHNOLOGY, Seymour House, Old Trafford, Manchester.—Principals, Charles Estcourt, F.I.C., F.C.S., &c., and Philip Anderson Estcourt, Ph.D. The course of instruction is especially intended for those who require a knowledge of Chemistry and Bacteriology bearing upon Sanitary matters. Chemical Technology is specially taught with a view to enable Medical Men and others engaged in Sanitary matters to understand the operations at the various works which may come under their control. Persons who desire to take up the branch of Chemical Engineering, including Electrical Engineering, will also have special opportunities of pursuing such studies.

THE MUNICIPAL SCHOOL OF TECHNOLOGY, Sackville Street, Manchester.—This fine building, which has been in partial occupation during the past session, is to be formally opened by the Prime Minister on October 15 next. It occupies an area of upwards of 6800 square yards, and is six floors in height. Its equipment, which is nearly complete, is on a scale of great magnitude. It comprises laboratories and workshops for Mechanical, Electrical, and Hydraulic Engineering, for the Textile industries, and for the industries included within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises, in addition to ample accommodation for pure Chemistry, laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity.

LEEDS TECHNICAL SCHOOL (in connection with the Leeds Institute of Science, Art, and Literature), Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in 40 subjects of Science and Technology, among which are:—Chemistry, Inorganic and Organic, Theoretical and Practical, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, and Mr. T. R. White, B.A.; Metallurgy, Theoretical and Practical, and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Magnetism and Electricity, and Practical Physics, by Mr. J. E. Tindall, B.A., B.Sc.; Botany, Lectures and Practical Work, by Mr. N. Walker; Photography, by Mr. S. E. Bottomley. Fees:—Lectures, from 2s. 6d. per Session; Laboratory work, from 2s. 6d. Systematic courses arranged for Pharmaceutical Students and for those engaged in Chemical Industries at composition fees. Session commences Sept. 15th. Prospectuses of various Classes free on application to the Secretary, Mr. Arthur Tait. Calendar of the Institute (164 pp.) post free 5d.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Messrs. W. Whitehouse, W. Rogers, and H. J. Tench; Botany, Mr. Sidney Phillips, Ph.C.; Latin, Mr. F. G. Griffiths, M.P.S. Day Classes in Chemistry and Physics, and Evening Classes in Chemistry, Physics, Botany, French, Latin, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. The School is recognised by the Examining Board of the Royal College of Surgeons and Physicians, as a centre for preparation in Chemistry and Physics. Session commences Monday, Sept. 15th. For other particulars and programme, apply Mr. G. F. Chell, Secretary.

CHEMISTRY AT THE BRITISH ASSOCIATION.

The President of Section B, Professor E. DIVERS, M.D., F.R.S., will deal with some aspects of the Atomic Theory in his address to the Section. The following papers, amongst others, will be read:—

- "Our present Knowledge of Aromatic Diazo-compounds," by Dr. G. T. Morgan.
 - "Reduced Benzene Derivatives containing a Single Nucleus," by Dr. A. W. Crossley.
 - "Present Synthetical Research on the Glucosides," and "The Synthetical Action of Enzymes," by Dr. E. F. Armstrong.
 - "The Alkylation of the Sugars," by Professor T. Purdie, F.R.S., and Dr. Irvine.
 - "The Colour of Iodine-containing Compounds," by Miss Ida Smedley.
 - "On Zirconium Hydrate and other Colloids from Elements of the Fourth Group," by Dr. J. H. Gladstone, F.R.S., and Mr. W. Hibbert.
 - "On some Optical Properties of Tellurium," by Dr. J. H. Gladstone, F.R.S.
 - "The Telluric Distribution of the Elements in relation to their Atomic Weights," by Mr. W. Ackroyd, F.I.C.
 - "The Undesirability of establishing Standard Analytical Methods," by Mr. B. Blount, F.I.C.
 - "The Action of Distilled Water on Lead," by Dr. F. Clowes.
 - "The Decomposition of Urea," by Dr. C. E. Fawsitt.
 - "On the Corrosion of Copper by Sea-water and on the Detection of Traces of Impurity in the Commercial Metal," by Dr. E. A. Letts.
 - "On Experiments to Ascertain the amount of Carbonic Anhydride Absorbed from Sea-water by Air," by Dr. E. A. Letts and Mr. W. Caldwell.
 - "On the Absorption of Ammonia from Water by Algæ," by Dr. E. A. Letts and Mr. J. S. Jotton.
- Professor D. Vorländer, of Halle, and Professor E. Knoevenagel, of Heidelberg, are expected to be present as guests of the Association.

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FACULTIES OF SCIENCE, ARTS, AND COMMERCE.

1902-3.

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Candidates, who must be Bachelors in Science of a British University, of not more than three years' standing, are required to send in their names on or before the 26th inst. to the SECRETARY, from whom further particulars may be obtained.

UNIVERSITY COLLEGE, LIVERPOOL.

DEPARTMENT OF CHEMISTRY.

The next Examination for the SHERIDAN MUSPRATT CHEMICAL SCHOLARSHIP, of the value of £50 per annum, tenable for two years, will be held in DECEMBER, 1902. Preference will be given to Students under twenty-three years of age on the 1st of January following the date of examination. Candidates must send in their names to the COLLEGE SECRETARY not later than November 15, 1902.

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MICHAELMAS TERM.—Monday, October 6, to Saturday, December 13.

LENT TERM.—Monday, January 5, to Saturday, April 4.

EASTER TERM.—Monday, April 27, to Saturday, July 25.

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Lecturer—FRANCIS E. FRANCIS, M.Sc., Ph.D.

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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2233.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BELFAST, 1902.

INAUGURAL ADDRESS OF THE PRESIDENT,
PROF. JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

THE members of an Association whose studies involve perpetual contemplation of settled law and ordered evolution, whose objects are to seek patiently for the truth of things and to extend the dominion of man over the forces of nature, are even more deeply pledged than other men to loyalty to the Crown and the Constitution which procure for them the essential conditions of calm security and social stability. I am confident that I express the sentiments of all now before me when I say that to our loyal respect for his high office we add a warmer feeling of loyalty and attachment to the person of our Gracious Sovereign. It is the peculiar felicity of the British Association that, since its foundation seventy-one years ago, it has always been easy and natural to cherish both these sentiments, which indeed can never be dissociated without peril. At this, our second meeting held under the present reign, these sentiments are realised all the more vividly, because, in common with the whole empire, we have recently passed through a period of acute apprehension, followed by the uplifting of a national deliverance. The splendid and imposing coronation ceremony which took place just a month ago was rendered doubly impressive both for the King and his people by the universal consciousness that it was also a service of thanksgiving for escape from imminent peril. In offering to His Majesty our most hearty congratulations upon his singularly rapid recovery from a dangerous illness, we rejoice to think that the nation has received gratifying evidence of the vigour of his constitution, and may, with confidence more assured than before, pray that he may have length of happy and prosperous days. No one in his wide dominions is more competent than the King to realise how much he owes, not only to the skill of his surgeons, but also to the equipment which has been placed in their hands as the combined result of scientific investigation in many and diverse directions. He has already displayed a profound and sagacious interest in the discovery of methods for dealing with some of the most intractable maladies that still baffle scientific penetration; nor can we doubt that this interest extends to other forms of scientific investigation, more directly connected with the amelioration of the lot of the healthy than with the relief of the sick. Hereditarily imposes obligations and also confers aptitude for their discharge. If His Majesty's royal mother throughout her long and beneficent reign set him a splendid example of devotion to the burdensome labours of State which must necessarily absorb the chief part of his energies, his father no less clearly indicated the great part he may play in the encouragement of science. Intelligent appreciation of scientific work and needs is not less but more necessary in the highest quarters to-day than it was forty-three years ago, when His Royal Highness the Prince Consort brought the matter before this Association in the following memorable passage in his Presidential Address:—"We may be justified, however, in hoping that by the gradual diffusion of science and its increasing recognition as a principal part of our national education, the public in general, no less than the legislature and the State, will more and more recognise the claims of science to their

attention; so that it may no longer require the begging box, but speak to the State like a favoured child to its parent, sure of his paternal solicitude for its welfare; that the State will recognise in science one of its elements of strength and prosperity, to protect which the clearest dictates of self-interest demand." Had this advice been seriously taken to heart and acted upon by the rulers of the nation at the time, what splendid results would have accrued to this country! We should not now be painfully groping in the dark after a system of national education. We should not be wasting money, and time more valuable than money, in building imitations of foreign educational superstructures before having put in solid foundations. We should not be hurriedly and distractedly casting about for a system of tactics after confrontation with the disciplined and co-ordinated forces of industry and science led and directed by the rulers of powerful States. Forty-three years ago we should have started fair had the Prince Consort's views prevailed. As it is, we have lost ground which it will tax even this nation's splendid reserves of individual initiative to recover. Although in this country the King rules, but does not govern, the Constitution and the structure of English society assure to him a very potent and far-reaching influence upon those who do govern. It is hardly possible to overrate the benefits that may accrue from his intelligent and continuous interest in the great problem of transforming his people into a scientifically educated nation. From this point of view we may congratulate ourselves that the heir to the Crown, following his family traditions, has already deduced from his own observations in different parts of the empire some very sound and valuable conclusions as to the national needs at the present day.

Griffith—Gilbert—Cornu.

The saddest yet the most sacred duty falling to us on such an occasion as the present is to pay our tribute to the memory of old comrades and fellow-workers whom we shall meet no more. We miss to-day a figure that has been familiar, conspicuous, and always congenial at the meetings of the British Association during the last forty years. Throughout the greater part of that period Mr. George Griffith discharged the onerous and often delicate duties of the assistant general secretary, not only with conscientious thoroughness and great ability, but also with urbanity, tact, and courtesy that endeared him to all. His years sat lightly upon him, and his undiminished alertness and vigour caused his sudden death to come upon us all with a shock of surprise as well as of pain and grief. The British Association owes him a debt of gratitude which must be so fully realised by every regular attender of our meetings that no poor words of mine are needed to quicken your sense of loss, or to add to the poignancy of your regret.

The British Association has to deplore the loss from among us of Sir Joseph Gilbert, a veteran who continued to the end of a long life to pursue his important and beneficent researches with untiring energy. The length of his services in the cause of science cannot be better indicated than by recalling the fact that he was one of the six past Presidents boasting fifty years' membership whose jubilee was celebrated by the Chemical Society in 1898. He was in fact an active member of that Society for over sixty years. Early in his career he devoted himself to a most important but at that time little cultivated field of research. He strove with conspicuous success to place the oldest of industries on a scientific basis, and to submit the complex conditions of agriculture to a systematic analysis. He studied the physiology of plant life in the open air, not with the object of penetrating the secrets of structure, but with the more directly utilitarian aim of establishing the conditions of successful and profitable cultivation. By a long series of experiments alike well conceived and laboriously carried out, he determined the effects of variation in soil, and its chemical treatment—in short, in all the unknown factors with which the

farmer previously had to deal according to empirical and local rules, roughly deduced from undigested experience by uncritical and rudimentary processes of inference. Gilbert had the faith, the insight, and the courage to devote his life to an investigation so difficult, so unpromising, and so unlikely to bring the rich rewards attainable by equal diligence in other directions, as to offer no attraction to the majority of men. The tabulated results of the Rothamsted experiments remain as a benefaction to mankind and a monument of indomitable and disinterested perseverance.

It is impossible for me in this place to offer more than the barest indication of the great place in contemporary science that has been vacated by the lamented death of Professor Alfred Cornu, who so worthily upheld the best traditions of scientific France. He was gifted in a high degree with the intellectual lucidity, the mastery of form, and the perspicuous method which characterised the best exponents of French thought in all departments of study. After a brilliant career as a student, he was chosen at the early age of twenty-six to fill one of the enviable positions more numerous in Paris than in London, the Professorship of Physics at the Ecole Polytechnique. In that post, which he occupied to the end of his life, he found what is probably the ideal combination for a man of science—leisure and material equipment for original research, together with that close and stimulating contact with practical affairs afforded by his duties as teacher in a great school, almost ranking as a department of State. Cornu was admirable alike in the use he made of his opportunities and in his manner of discharging his duties. He was at once a great investigator and a great teacher. I shall not even attempt a summary, which at the best must be very imperfect, of his brilliant achievements in optics, the study of his predilection, in electricity, in acoustics, and in the field of physics generally. As a proof of the great estimation in which he was held, it is sufficient to remind you that he had filled the highest presidential offices in French scientific societies, and that he was a foreign member of our Royal Society and a recipient of its Rumford medal. In this country he had many friends, attracted no less by his personal and social qualities than by his commanding abilities. Some of those here present may remember his appearance a few years ago at the Royal Institution, and more recently his delivery of the Rede Lecture at Cambridge, when the University conferred upon him the honorary degree of Doctor of Science. His death has inflicted a heavy blow upon our generation, upon France, and upon the world.

The Progress of Belfast.

A great man has observed that the "intelligent anticipation of events before they occur" is a factor of some importance in human affairs. One may suppose that intelligent anticipation had something to do with the choice of Belfast as the meeting-place of the British Association this year. Or, if it had not, then it must be admitted that circumstances have conspired, as they occasionally do, to render the actual selection peculiarly felicitous. Belfast has perennial claims, of a kind that cannot easily be surpassed, to be the scene of a great scientific gathering—claims founded upon its scientific traditions and upon the conspicuous energy and success with which its citizens have prosecuted in various directions the application of science to the purposes of life. It is but the other day that the whole nation deplored at the grave of Lord Dufferin the loss of one of the most distinguished and most versatile public servants of the age. That great statesman and near neighbour of Belfast was a typical expression of the qualities and the spirit which have made Belfast what it is, and have enabled Ireland, in spite of all drawbacks, to play a great part in the Empire. I look round on your thriving and progressive city giving evidence of an enormous aggregate of industrial efforts intelligently organised and directed for the building up of a sound social fabric. I find that your great industries are

interlinked and interwoven with the whole economic framework of the Empire, and that you are silently and irresistibly compelled to harmonious co-operation by practical considerations acting upon the whole community. It is here that I look for the real Ireland, the Ireland of the future. We cannot trace with precision the laws that govern the appearance of eminent men, but we may at least learn from history that they do not spring from every soil. They do not appear among decadent races or in ages of retrogression. They are the fine flower of the practical intellect of the nation working studiously and patiently in accordance with the great laws of conduct. In the manifold activities of Belfast we have a splendid manifestation of individual energy working necessarily, even if not altogether consciously, for the national good. In great Irishmen like Lord Dufferin and Lord Roberts, giving their best energies for the defence of the nation by diplomacy or by war, we have complimentary evidence enough to reassure the most timid concerning the real direction of Irish energies and the vital nature of Irish solidarity with the rest of the Empire.

Belfast has played a prominent part in a transaction of a somewhat special and significant kind, which has proved not a little confusing and startling to the easy-going public. The significance of the shipping combination lies in the light it throws on the conditions and tendencies which make such things possible, if not even inevitable. It is an event forcibly illustrating the declaration of his Royal Highness the Prince of Wales, that the nation must "wake up" if it hopes to face its growing responsibilities. Belfast may plead with some justice that it, at least, has never gone to sleep. In various directions an immense advance has been effected during the twenty-eight years that have elapsed since the last visit of the British Association. Belfast has become first a city and then a county, and now ranks as one of the eight largest cities in the United Kingdom. Its municipal area has been considerably extended, and its population has increased by something like 75 per cent. It has not only been extended, but improved and beautified in a manner which very few places can match, and which probably none can surpass. Fine new thoroughfares, adorned with admirable public institutions, have been run through areas once covered with crowded and squalid buildings. Compared with the early fifties, when iron shipbuilding was begun on a very modest scale, the customs collected at the port have increased tenfold. Since the introduction of the power-loom, about 1850, Belfast has distanced all rivals in the linen industry, which continues to flourish notwithstanding the fact that most of the raw material is now imported, instead of being produced, as in former times, in Ulster. Extensive improvements have been carried out in the port at a cost of several millions, and have been fully justified by a very great expansion of trade. These few bare facts suffice to indicate broadly the immense strides taken by Belfast in the last two decades. For an Association that exists for the advancement of science it is stimulating and encouraging to find itself in the midst of a vigorous community, successfully applying knowledge to the ultimate purpose of all human effort, the amelioration of the common lot by an ever-increasing mastery of the powers and resources of Nature.

Tyndall and Evolution.

The Presidential Address delivered by Tyndall in this city twenty-eight years ago will always rank as an epoch-making deliverance. Of all the men of the time, Tyndall was one of the best equipped for the presentation of a vast and complicated scientific subject to the mass of his fellow-men. Gifted with the powers of a many-sided original investigator, he had at the same time devoted much of his time to an earnest study of philosophy, and his literary and oratorical powers, coupled with a fine poetic instinct, were qualifications which placed him in the front rank of the scientific representatives of the later Victorian epoch, and constituted him an exceptionally endowed exponent of scientific thought. In the Belfast dis-

course Tyndall dealt with the changing aspects of the long unsettled horizon of human thought, at last illuminated by the sunrise of the doctrine of evolution. The consummate art with which he marshalled his scientific forces for the purpose of effecting conviction of the general truth of the doctrine has rarely been surpassed. The courage, the lucidity, the grasp of principles, the moral enthusiasm with which he treated his great theme, have powerfully aided in effecting a great intellectual conquest, and the victory assuredly ought to engender no regrets.

Tyndall's views as a strenuous supporter and believer in the theory of evolution were naturally essentially optimistic. He had no sympathy with the lugubrious pessimistic philosophy whose disciples are for ever intent on administering rebuke to scientific workers by reminding them that, however much knowledge man may have acquired, it is as nothing compared with the immensity of his ignorance. That truth is indeed never adequately realised except by the man of science, to whom it is brought home by repeated experience of the fact that his most promising excursions into the unknown are invariably terminated by barriers which, for the time at least, are insurmountable. He who has never made such excursions with patient labour may indeed prattle about the vastness of the unknown, but he does so without real sincerity or intimate conviction. His tacit, if not his avowed, contention is, that since we can never know all, it is not worth while to seek to know more; and that in the profundity of his ignorance he has the right to people the unexplored spaces with the phantoms of his vain imagining. The man of science, on the contrary, finds in the extent of his ignorance a perpetual incentive to further exertion, and in the mysteries that surround him a continual invitation, nay, more, an inexorable mandate. Tyndall's writings abundantly prove that he had faced the great problems of man's existence with that calm intellectual courage, the lack of which goes very far to explain the nervous dogmatism of nescience. Just because he had done this, because he had, as it were, mapped out the boundaries between what is knowable though not yet known and what must remain for ever unknowable to man, he did not hesitate to place implicit reliance on the progress of which man is capable, through the exercise of patient and persistent research. In Tyndall's scheme of thought the chief dicta were the strict division of the world of knowledge from that of emotion, and the lifting of life by throwing overboard the malign residuum of dogmatism, fanaticism, and intolerance, thereby stimulating and nourishing a plastic vigour of intellect. His cry was "Commotion before stagnation, the leap of the torrent before the stillness of the swamp."

His successors have no longer any need to repeat those significant words, "We claim and we shall wrest from theology the entire domain of cosmological theory." The claim has been practically, though often unconsciously, conceded. Tyndall's dictum, "Every system must be plastic to the extent that the growth of knowledge demands," struck a note that was too often absent from the heated discussions of days that now seem so strangely remote. His honourable admissions that, after all that had been achieved by the developmental theory, "the whole process of evolution is the manifestation of a power absolutely inscrutable to the intellect of man," shows how willingly he acknowledged the necessary limits of scientific inquiry. This reservation did not prevent him from expressing the conviction forced upon him by the pressure of intellectual necessity, after exhaustive consideration of the known relations of living things, that matter in itself must be regarded as containing the promise and potency of all terrestrial life. Bacon in his day said very much the same thing: "He that will know the properties and proceedings of matter should comprehend in his understanding the sum of all things, which have been, which are, and which shall be, although no knowledge can extend so far as to singular and individual beings." Tyndall's conclusion was at the time thought to be based on a too

insecure projection into the unknown, and some even regarded such an expansion of the crude properties of matter as totally unwarranted. Yet Tyndall was certainly no materialist in the ordinary acceptance of the term. It is true his arguments, like all arguments, were capable of being distorted, especially when taken out of their context, and the address became in this way an easy prey for hostile criticism. The glowing rhetoric that gave charm to his discourse and the poetic similes that clothed the dry bones of his close-woven logic were attacked by a veritable broadside of critical artillery. At the present day these would be considered as only appropriate artistic embellishments, so great is the unconscious change wrought in our surroundings. It must be remembered that, while Tyndall discussed the evolutionary problem from many points of view, he took up the position of a practical disciple of Nature dealing with the known experimental and observational realities of physical inquiry. Thus he accepted as fundamental concepts the atomic theory, together with the capacity of the atom to be the vehicle or repository of energy, and the grand generalisation of the conservation of energy. Without the former, Tyndall doubted whether it would be possible to frame a theory of the material universe; and as to the latter he recognised its radical significance in that the ultimate philosophical issues therein involved were as yet but dimly seen. That such generalisations are provisionally accepted does not mean that science is not alive to the possibility that what may now be regarded as fundamental may in future be superseded or absorbed by a wider generalisation. It is only the poverty of language and the necessity for compendious expression that oblige the man of science to resort to metaphor and to speak of the Laws of Nature. In reality, he does not pretend to formulate any laws for Nature, since to do so would be to assume a knowledge of the inscrutable cause from which alone such laws could emanate. When he speaks of a "law of Nature," he simply indicates a sequence of events which, so far as his experience goes, is invariable, and which therefore enables him to predict, to a certain extent, what will happen in given circumstances. But, however seemingly bold may be the speculation in which he permits himself to indulge, he does not claim for his best hypothesis more than provisional validity. He does not forget that to-morrow may bring a new experience compelling him to re-cast the hypothesis of to-day. This plasticity of scientific thought, depending upon reverent recognition of the vastness of the unknown, is oddly made a matter of reproach by the very people who harp upon the limitations of human knowledge. Yet the essential condition of progress is that we should generalise to the best of our ability from the experience at command, treat our theory as provisionally true, endeavour to the best of our power to reconcile with it all the new facts we discover, and abandon or modify it when it ceases to afford a coherent explanation of new experience. That procedure is far as are the poles asunder from the presumptuous attempt to travel beyond the study of secondary causes. Any discussion as to whether matter or energy was the true reality would have appeared to Tyndall as a futile metaphysical disputation, which being completely dissociated from verified experience, would lead to nothing. No explanation was attempted by him of the origin of the bodies we call elements, nor how some of such bodies came to be compounded into complex groupings and built up into special structures with which, so far as we know, the phenomena characteristic of life are invariably associated. The evolutionary doctrine leads us to the conclusion that life, such as we know it, has only been possible during a short period of the world's history, and seems equally destined to disappear in the remote future; but it postulates the existence of a material universe endowed with an infinity of powers and properties, the origin of which it does not pretend to account for. The enigma at both ends of the scale Tyndall admitted, and the futility of attempting to answer such

questions he fully recognised. Nevertheless, Tyndall did not mean that the man of science should be debarred from speculating as to the possible nature of the simplest forms of matter or the mode in which life may have originated on this planet. Lord Kelvin, in his Presidential Address, put the position admirably when he said "Science is bound by the everlasting law of honour to face fearlessly every problem that can fairly be presented to it. If a probable solution consistent with the ordinary course of Nature can be found, we must not invoke an abnormal act of Creative Power"; and in illustration he forthwith proceeded to express his conviction that from time immemorial many worlds of life besides our own have existed, and that "it is not an unscientific hypothesis that life originated on this earth through the moss-grown fragments from the ruins of another world." In spite of the great progress made in science, it is curious to notice the occasional recrudescence of metaphysical dogma. For instance, there is a school which does not hesitate to revive ancient mystifications in order to show that matter and energy can be shattered by philosophical arguments, and have no objective reality. Science is at once more humble and more reverent. She confesses her ignorance of the ultimate nature of matter, of the ultimate nature of energy, and still more of the origin and ultimate synthesis of the two. She is content with her patient investigation of secondary causes, and glad to know that since Tyndall spoke in Belfast she has made great additions to the knowledge of general molecular mechanism, and especially of synthetic artifice in the domain of organic chemistry, though the more exhaustive acquaintance gained only forces us the more to acquiesce in acknowledging the inscrutable mystery of matter. Our conception of the power and potency of matter has grown in little more than a quarter of a century to much more imposing dimensions, and the outlook for the future assuredly suggests the increasing acceleration of our rate of progress. For the impetus he gave to scientific work and thought, and for his fine series of researches chiefly directed to what Newton called the more secret and noble works of Nature within the corpuscles, the world owes Tyndall a debt of gratitude. It is well that his memory should be held in perennial respect, especially in the land of his birth.

The Endowment of Education.

These are days of munificent benefactions to science and education, which, however, are greater and more numerous in other countries than in our own. Splendid as they are, it may be doubted, if we take into account the change in the value of money, the enormous increase of population, and the utility of science to the builders of colossal fortunes, whether they bear comparison with the efforts of earlier days. But the habit of endowing science was so long in practical abeyance that every evidence of its resumption is matter for sincere congratulation. Mr. Cecil Rhodes has dedicated a very large sum of money to the advancement of education, though the means he has chosen are perhaps not the most effective. It must be remembered that his aims were political as much as educational. He had the noble and worthy ambition to promote enduring friendship between the great English-speaking communities of the world, and knowing the strength of college ties he conceived that this end might be greatly furthered by bringing together at an English university the men who would presumably have much to do in later life with the influencing of opinion, or even with the direction of policy. It has been held by some a striking tribute to Oxford that a man but little given to academic pursuits or modes of thought should think it a matter of high importance to bring men from our colonies or even from Germany, to submit to the formative influences of that ancient seat of learning. But this is perhaps reading Mr. Rhodes backwards. He shows his affectionate recollection of his college days by his gift to Oriel. But, apart from the main idea of fostering good relations between those who will presumably be influential in England, in the

Colonies, and in the United States, Mr. Rhodes was probably influenced also by the hope that the influx of strangers would help to broaden Oxford notions and to procure revision of conventional arrangements.

Dr. Andrew Carnegie's endowment of Scottish universities, as modified by him in deference to expert advice, is a more direct benefit to the higher education. For while Mr. Rhodes has only enabled young men to get what Oxford has to give, Dr. Carnegie has also enabled his trustees powerfully to augment and improve the teaching equipment of the universities themselves. At the same time he has provided as far as possible for the enduring usefulness of his money. His trustees form a permanent body external to the universities, which, while possessing no power of direct control, must always, as holder of the purse-strings, be in a position to offer independent and weighty criticisms. More recently, Dr. Carnegie has devoted an equal sum of ten million dollars to the foundation of a Carnegie Institution in Washington. Here again he has been guided by the same ideas. He has neither founded a university nor handed over the money to any existing university. He has created a permanent trust charged with the duty of watching educational efforts and helping them from the outside according to the best judgment that can be formed in the circumstances of the moment. Its aims are to be—to promote original research; to discover the exceptional man in every department of study, whether inside or outside of the schools, and to enable him to make his special study his life-work; to increase facilities for higher education; to aid and stimulate the universities and other educational institutions; to assist students who may prefer to study at Washington; and to ensure prompt publication of scientific discoveries. The general purpose of the founder is to secure, if possible, for the United States leadership in the domain of discovery and the utilisation of new forces for the benefit of man. Nothing will more powerfully further this end than attention to the injunction to lay hold of the exceptional man whenever and wherever he may be found, and, having got him, to enable him to carry on the work for which he seems specially designed. That means, I imagine, a scouring of the old world, as well as of the new, for the best men in every department of study—in fact, an assiduous collecting of brains similar to the collecting of rare books and works of art which Americans are now carrying on in so lavish a manner. As in diplomacy and war, so in science, we owe our reputation, and no small part of our prosperity, to exceptional men; and that we do not enjoy these things in fuller measure we owe to our lack of an army of well-trained ordinary men capable of utilising their ideas. Our exceptional men have too often worked in obscurity, without recognition from a public too imperfectly instructed to guess at their greatness, without assistance from a State governed largely by dialecticians, and without help from academic authorities hidebound by the pedantries of medieval scholasticism. For such men we have to wait upon the will of Heaven. Even Dr. Carnegie will not always find them when they are wanted. But what can be done in that direction will be done by institutions like Dr. Carnegie's, and for the benefit of the nation that possesses them in greatest abundance and uses them most intelligently. When contemplating these splendid endowments of learning, it occurred to me that it would be interesting to find out exactly what some definite quantity of scientific achievements has cost in hard cash. In an article by Carl Snyder in the January number of the *North American Review*, entitled, "America's Inferior Place in the Scientific World," I found the statement that "it would be hardly too much to say that during the hundred years of its existence the Royal Institution alone has done more for English science than all of the English universities put together. This is certainly true with regard to British industry, for it was here that the discoveries of Faraday were made." I was emboldened by this estimate from a distant and impartial observer to

do, what otherwise I might have shrunk from doing, and to take the Royal Institution—after all, the foundation of an American citizen, Count Rumford—as the basis of my inquiry. The work done at the Royal Institution during the past hundred years is a fairly definite quantity in the mind of every man really conversant with scientific affairs. I have obtained from the books accurate statistics of the total expenditure on experimental inquiry and public demonstrations for the whole of the nineteenth century. The items are:—

Professors' salaries—Physics and Chemistry ..	£54,600
Laboratory expenditure	24,430
Assistants' salaries	21,590

Total for one hundred years £100,620

In addition, the members and friends of the Institution have contributed to a fund for exceptional expenditure for Experimental Research the sum of £9580. It should also be mentioned that a Civil List pension of £300 was granted to Faraday in 1853, and was continued during twenty-seven years of active work and five years of retirement. Thirty-two years in all, at £300 a year, make a sum of £9600, representing the national donation, which, added to the amount of expenditure just stated, brings up the total cost of a century of scientific work in the laboratories of the Royal Institution, together with public demonstrations, to £119,800, or an average of £1200 per annum. I think if you recall the names and achievements of Young, Davy, Faraday, and Tyndall, you will come to the conclusion that the exceptional man is about the cheapest of natural products. It is a popular fallacy that the Royal Institution is handsomely endowed. On the contrary, it has often been in financial straits; and since its foundation by Count Rumford its only considerable bequests have been one from Thomas G. Hodgkins, an American citizen, for Experimental Research, and that of John Fuller for endowing with £95 a year the chairs of Chemistry and Physiology. In this connection the Davy-Faraday Laboratory, founded by the liberality of Dr. Ludwig Mond, will naturally occur to many minds. But though affiliated to the Royal Institution, with, I hope, reciprocal indirect advantages, that Laboratory is financially independent and its endowments are devoted to its own special purpose, which is to provide opportunity to prosecute independent research for worthy and approved applicants of all nationalities. The main reliance of the Royal Institution has always been, and still remains, upon the contributions of its members, and upon corresponding sacrifices in the form of time and labour by its professors. It may be doubted whether we can reasonably count upon a succession of scientific men able and willing to make sacrifices which the conditions of modern life tend to render increasingly burdensome. Modern science is in fact in something of a dilemma. Devotion to abstract research upon small means is becoming always harder to maintain, while at the same time the number of wealthy independent searchers after truth, and patrons of science of the style of Joule, Spottiswoode, and De la Rue, is apparently becoming smaller. The installations required by the refinements of modern science are continually becoming more costly, so that upon all grounds it would appear that without endowments of the kind provided by Dr. Carnegie the outlook for disinterested research is rather dark. On the other hand, these endowments, unless carefully administered, might obviously tend to impair the single-minded devotion to the search after truth for its own sake, to which science has owed almost every memorable advance made in the past. The Carnegie Institute will dispose in a year of as much money as the members of the Royal Institution have expended in a century upon its purely scientific work. It will at least be interesting to note how far the output of high-class scientific work corresponds to the hundredfold application of money to its production. Nor will it be of less interest to the people of this country to observe the results obtained from that

moiey of Dr. Carnegie's gift to Scotland which is to be applied to the promotion of scientific research.

Applied Chemistry, English and Foreign.

The Diplomatic and Consular reports published from time to time by the Foreign Office are usually too belated to be of much use to business men, but they sometimes contain information concerning what is done in foreign countries which affords food for reflection. One of these reports, issued a year ago, gives a very good account of the German arrangements and provisions for scientific training, and of the enormous commercial demand for the services of men who have passed successfully through the Universities and Technical High Schools, as well as of the wealth that has accrued to Germany through the systematic application of scientific proficiency to the ordinary business of life.

Taking these points in their order, I have thought it a matter of great interest to obtain a comparative view of chemical equipment in this country and in Germany, and I am indebted to Professor Henderson of Glasgow, who last year became the secretary of a committee of this Association of which Professor Armstrong is chairman, for statistics referring to this country, which enable a comparison to be broadly made. The author of the consular report estimates that in 1901 there were 4500 trained chemists employed in German works, the number having risen to this point from 1700 employed twenty-five years earlier. It is difficult to give perfectly accurate figures for this country, but a liberal estimate places the number of works chemists at 1500, while at the very outside it cannot be put higher than somewhere between 1500 and 2000. In other words, we cannot show in the United Kingdom, notwithstanding the immense range of the chemical industries in which we once stood prominent, more than one-third of the professional staff employed in Germany. It may perhaps be thought or hoped that we make up in quality for our defect in quantity, but unfortunately this is not the case. On the contrary, the German chemists are, on the average, as superior in technical training and acquirements as they are numerically. Details are given in the report of the training of 633 chemists employed in German works. Of these, 69 per cent hold the degree of Ph.D., about 10 per cent hold the diploma of a Technical High School, and about 5 per cent hold both qualifications. That is to say, 84 per cent have received a thoroughly systematic and complete chemical training, and 74 per cent of these add the advantages of a university career. Compare with this the information furnished by 500 chemists in British works. Of these, only 21 per cent are graduates, while about 10 per cent hold the diploma of a college. Putting the case as high as we can, and ignoring the more practical and thorough training of the German universities, which give their degrees for work done, and not for questions asked and answered on paper, we have only 31 per cent of systematically trained chemists against 84 per cent in German works. It ought to be mentioned that about 21 per cent of the 500 are Fellows or Associates of the Institute of Chemistry, whatever that may amount to in practice, but of these a very large number have already been accounted for under the heads of graduates and holders of diplomas. These figures, which I suspect are much too favourable on the British side, unmistakably point to the prevalence among employers in this country of the antiquated adherence to rule of thumb, which is at the root of much of the backwardness we have to deplore. It hardly needs to be pointed out to such an audience as the present that chemists who are neither graduates of a university nor holders of a diploma from a technical college, may be competent to carry on existing processes according to traditional methods, but are very unlikely to effect substantial improvements, or to invent new and more efficient processes. I am very far from denying that here and there an individual may be found whose exceptional ability enables him to triumph over all defects of training. But in all educational matters it is the average

man whom we have to consider, and the average ability which we have to develop. Now, to take the second point—the actual money value of the industries carried on in Germany by an army of workers both quantitatively and qualitatively so superior to our own. The Consular report estimates the whole value of German chemical industries at not less than fifty millions sterling per annum. These industries have sprung up within the last seventy years, and have received enormous expansion during the last thirty. They are, moreover, very largely founded upon basic discoveries made by English chemists, but never properly appreciated or scientifically developed in the land of their birth. I will place before you some figures showing the growth of a single firm engaged in a single one of these industries—the utilisation of coal-tar for the production of drugs, perfumes, and colouring-matters of every conceivable shade. The firm of Friedrich Bayer and Co. employed in 1875, 119 workmen. The number has more than doubled itself every five years, and in May of this year that firm employed 5000 workmen, 160 chemists, 260 engineers and mechanics, and 680 clerks. For many years past it has regularly paid 18 per cent on the ordinary shares, which this year has risen to 20 per cent; and in addition, in common with other and even larger concerns in the same industry, has paid out of profits for immense extensions usually charged to capital account. There is one of these factories the works and plant of which stand in the books at £1,500,000, while the money actually sunk in them approaches to £5,000,000. In other words, the practical monopoly enjoyed by the German manufacturers enables them to exact huge profits from the rest of the world, and to establish a position which, financially as well as scientifically, is almost unassailable. I must repeat that the fundamental discoveries upon which this gigantic industry is built were made in this country, and were practically developed to a certain extent by their authors. But in spite of the abundance and cheapness of the raw material, and in spite of the evidence that it could be most remuneratively worked up, these men founded no school and had practically no successors. The colours they made were driven out of the field by newer and better colours made from their stuff by the development of their ideas, but these improved colours were made in Germany and not in England. Now what is the explanation of this extraordinary and disastrous phenomenon? I give it in a word—want of education. We had the material in abundance when other nations had comparatively little. We had the capital and we had the brains, for we originated the whole thing. But we did not possess the diffused education without which the ideas of men of genius cannot fructify beyond the limited scope of an individual. I am aware that our patent laws are sometimes held responsible. Well, they are a contributory cause; but it must be remembered that other nations with patent laws as protective as could be desired have not developed the colour industry. The patent laws have only contributed in a secondary degree, and if the patent laws have been bad the reason for their badness is again want of education. Make them as bad as you choose, and you only prove that the men who made them, and the public whom these men try to please, were misled by theories instead of being conversant with fact and logic. But the root of the mischief is not in the patent laws or in any legislation whatever. It is in the want of education among our so-called educated classes, and secondarily among the workmen on whom these depend. It is in the abundance of men of ordinary plodding ability, thoroughly trained and methodically directed, that Germany at present has so commanding an advantage. It is the failure of our schools to turn out, and of our manufacturers to demand, men of this kind, which explains our loss of some valuable industries and our precarious hold upon others. Let no one imagine for a moment that this deficiency can be remedied by any amount of that technical training which is now the fashionable nostrum. It is an excellent thing,

no doubt, but it must rest upon a foundation of general training. Mental habits are formed for good or evil long before men go to the technical schools. We have to begin at the beginning: we have to train the population from the first to think correctly and logically, to deal at first hand with facts, and to evolve, each one for himself, the solution of a problem put before him, instead of learning by rote the solution given by somebody else. There are plenty of chemists turned out, even by our Universities, who would be of no use to Bayer and Co. They are chockfull of formulæ, they can recite theories, and they know text-books by heart; but put them to solve a new problem, freshly arisen in the laboratory, and you will find that their learning is all dead. It has not become a vital part of their mental equipment, and they are floored by the first emergence of the unexpected. The men who escape this mental barrenness are men who were somehow or other taught to think long before they went to the university. To my mind, the really appalling thing is not that the Germans have seized this or the other industry, or even that they may have seized upon a dozen industries. It is that the German population has reached a point of general training and specialised equipment which it will take us two generations of hard and intelligently directed educational work to attain. It is that Germany possesses a national weapon of precision which must give her an enormous initial advantage in any and every contest depending upon disciplined and methodised intellect.

(To be continued).

THE RADIO-ACTIVITY OF THORIUM COMPOUNDS.*

II. THE CAUSE AND NATURE OF RADIO-ACTIVITY.

By E. RUTHERFORD, M.A., D.Sc.,
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and
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(Continued from p. 101).

7. The Place of Emanating Power in the Radio-activity of Thorium.

TURNING from radio-active solids to gases which manifest this property, a great many of the very puzzling results obtained in the investigation of the radio-active emanation produced by thorium compounds can now also be simply explained. This section is devoted to this purpose and to further work that has been done in order to more exactly determine the place of emanating power in the radio-activity of thorium.

It was shown that the solutions from which thorium hydroxide had been precipitated by ammonia possessed about as much emanating power as the solutions from which they were prepared, while the precipitated hydroxide in all cases but one were more or less completely de-emanated, but spontaneously regained their normal value with lapse of time. It will be recalled that in one solitary instance that could not be repeated (*Trans. Chem. Soc.*, 1902, p. 344; *CHEMICAL NEWS*, vol. lxxv., p. 306) the hydroxide possessed an abnormally high emanating power, decaying to nearly normal value in fourteen days. This can now be explained. The thorium was first partly precipitated as thorium carbonate by means of sodium carbonate, and nitric acid added to re-dissolve a part. Under these circumstances all the ThX remains in solution, and on adding ammonia the thorium only should be precipitated, which, as always occurred when the experiment was repeated, ought to be more or less free from emanating power. But if as apparently happened in the experimental case, care was not taken to boil off all the carbon dioxide produced before adding ammonia, the latter would re-form a carbonate which completely pre-

* Communicated by the Authors.

precipitates both ThX and thorium. Hence the small hydroxide fraction contained all the ThX originally present, and possessed a high emanating power decaying to normal value with time. The fact that the carbonate fraction in this same experiment behaved abnormally, and did *not* recover its emanating power, is more difficult to explain, and the point will be reverted to later.

In further explanation of the results then obtained, it is only necessary to point out that since emanating power and not radio-activity was the first object of the investigation, any measurements of the latter, especially in the earlier part of the paper, were, as a rule, performed long after the specimens had been prepared; *i.e.*, after they had regained their normal values. In some cases if these measurements had been made immediately after preparation the results would have doubtless been different.

The conclusion was arrived at that emanating power was the manifestation of a dynamical change of the nature of a chemical reaction, rather than a function of matter in the static state, even before it was known that the emanating material, ThX, was being continuously reproduced. The latter discovery, however, enables a fairly complete explanation of the phenomenon to be given.

On resuming the work after the Christmas vacation, it was found that, on the one hand, some concentrated filtrates possessing high emanating power originally had completely lost it with lapse of time. On the other hand, the emanating power of almost all of the numerous samples of thorium hydroxide and carbonate prepared had recovered to about the same value, *viz.*, between three and four times that of thorium oxide.

The rate of decay of the emanating power of ThX, and the recovery of this property by the thorium from which it had been separated, were then investigated in parallel with the similar experiments on radio-activity already described. One quarter of the concentrated filtrate used for the latter purpose was taken, and the decrease of its emanating power with time measured. The increase of emanating power of the thorium hydroxide from which it had been prepared was also measured. The curves (Fig. 3) express the results. The decay curve is merely approximate; for it is not easy to accurately take the emanating power of a liquid without special arrangements to ensure the constancy of the air current and the shaking of the solution. The experiments, although merely approximate, bear out the conclusion that emanating power decays and recovers according to the same law as the radio-activity of ThX, and that it is therefore one of the properties of the latter and not of thorium. If care be taken to remove the ThX, the thorium almost entirely loses its emanating power. The small fraction that remains—often only a few per cent of the maximum—can be accounted for by the reproduction of ThX during the time taken to dry the precipitate. The decay curve given, so far as it can be relied on, shows that the emanating power of ThX at any instant is proportional to its radio-activity.

It was shown in the first paper that the emanation consisted of a chemically inert gas continuously emitted from thorium compounds. The results, therefore, find their simplest expression on the view that, just as a chemical change is proceeding in thorium whereby a non-thorium material is produced, so the latter undergoes a further reaction, giving rise to a gaseous product which in the radio-active state constitutes the emanation.

It will be seen at once that this secondary change is of a different kind from the primary, for it is affected apparently by the conditions in a very marked manner. It was shown that moisture, the state of aggregation and temperature, influenced the value of emanating power. From -80° to a red-heat the latter regularly increases in the ratio of 1:40 in the case of thorium oxide, while the ratio between the values for thorium nitrate in the solid state and in solution is as 1:200. The secondary reaction appears, therefore, at first sight much more nearly allied to ordinary chemical reaction than the primary. It must

not be forgotten, however, that the laws controlling the manifestation of the two phenomena—radio-activity and emanating power—are of necessity very different. In the former we deal with the intensity of radiations emitted by a solid, in the latter with the rate of escape of a gas into the surrounding air from either a solid or a liquid. Since this gas is detected by its radio-activity, and this decays extremely rapidly with time, a very slight delay in the rate of its escape will enormously affect the experimental value obtained for emanating power. It is possible that this cause is sufficient to account for the results obtained at different temperatures and with solids and liquids. De-emanation by ignition on this view would mean that at a certain temperature the crystalline form of thoria is permanently altered in such a way that the emanation is delayed in its escape.

On the other hand, it is now well established by experiment that sometimes thorium compounds de-emanated chemically by removal of ThX do not recover their normal emanating power with time, but remain constant at a lower value. The carbonate mentioned in the last paper, and already referred to, is an example of this; for it possessed hardly any emanating power until it was again dissolved and precipitated. On one occasion two samples of hydroxide prepared from different nitrates were tested together for rise of emanating power. That of the one rose normally to its maximum (as in Fig. 3), which was twenty times the minimum. The other started from the same minimum, but rose to a maximum only one-fourth as great. When the experiment was repeated under the same conditions, using the same sample of nitrate, the compound behaved normally. It thus appears that the emanation can be almost entirely prevented from escaping in the radio-active state in some cases, and partially prevented in others, where no visible peculiarity of physical condition exists, and where other preparations similarly prepared behave normally.

The question is further complicated by the property possessed by the emanation of exciting radio-activity on *all* surfaces with which it comes into contact. This process must be going on in the matter of the thorium compound itself, and it will be shown (Section 8) that this effect contributes an important quota to the total radio-activity of the compound. It seemed reasonable to suppose that the effect will be the greater, the less emanation succeeds in escaping in the radio-active state, and therefore that de-emanated compounds should possess a greater proportion of excited radio-activity than those with high emanating power. This conclusion was tested by converting a specimen of thorium carbonate with an emanating power five times that of ordinary thoria into oxide, and de-emanating by intense ignition. The energy that before escaped in the form of emanation is now all but a few per cent prevented from escaping. The radio-activity of the oxide so prepared rose in the first three days about 30 per cent of its original amount, and there thus seem to be grounds for the view that the excited radio-activity will contribute a much greater effect in a non-emanating thorium compound than in one possessing great emanating power. Additional confirmation of this view is to be found in the nature of the radiations emitted by the two classes of compounds (Section 10).

It will be seen that the phenomenon is too complicated to allow of an answer at the present stage to the question whether the secondary change which produces the emanation is, like the primary, independent of the conditions or not.

8. The Initial Portions of the Curves of Decay and Recovery.

The curves of the recovery and decay of the activities of thorium and ThX with time suggested the explanation that the radio-activity of thorium was being maintained by the production of ThX at a constant rate. Before this can be considered rigidly established two outstanding points remain to be cleared up:—1. What is the meaning

of the early portion of the curves? The recovery curve drops before it rises, and the decay curve rises before it drops. 2. Why does not the removal of ThX render thorium completely inactive? A large proportion of the original radio-activity remains after the removal of ThX.

A study of the curves (Fig. 1) shows that in each case a double action is probably at work. It must be supposed that the normal decay and recovery are taking place, but are being masked by a simultaneous rise and decay from causes unknown. From what is known of thorium radio-activity it was surmised that an action might be taking place similar to that effected by the emanation of exciting radio-activity on surrounding inactive matter. On this view the residual activity of thorium might consist in whole or in part of a secondary or excited radio-activity produced on the whole mass of the thorium compound by its association with the ThX. The drop in the recovery curve on this view would be due to the decay of this excited radio-activity proceeding simultaneously with and at first reversing the effect of the regeneration of ThX. The rise of the decay curve would be the increase due to the ThX exciting activity on the matter with which it is associated, the increase from this cause being greater than the decrease due to the decay of the activity of the ThX. It is easy to put this hypothesis to experimental test. If the ThX is removed from the thorium as soon as it is formed over a sufficient period, the former will be prevented from exciting activity on the latter, and that already excited will decay spontaneously. The experiment was therefore performed. A quantity of nitrate was precipitated as hydroxide in the usual way to remove ThX, the precipitate re-dissolved in nitric acid, and again precipitated after a certain interval. From time to time a portion of the hydroxide was removed, and its radio-activity tested. In this way the thorium was precipitated in all twenty-three times in a period of nine days, and the radio-activity reduced to a constant minimum. The following table shows the results:—

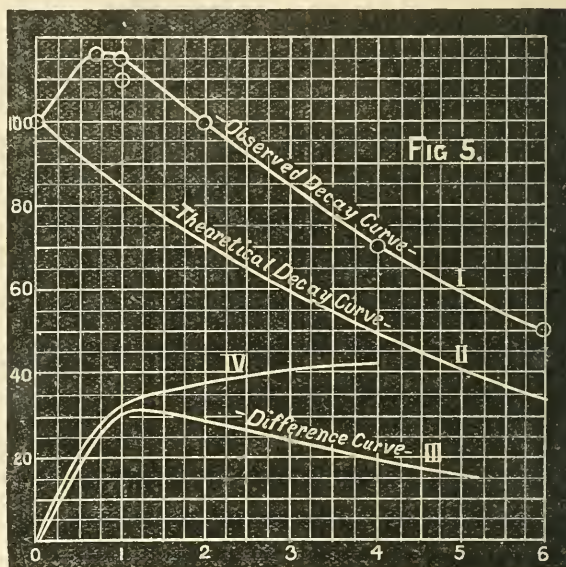
After precipitations—	Activity of hydroxide.
At three intervals of twenty-four hours	39 per cent
At three more intervals each of twenty-four hours, and three more each of eight hours.. . . .	22 per cent
At three more each of eight hours ..	24 per cent
At six more each of four hours ..	25 per cent

The constant minimum thus attained of about 25 per cent the original activity is thus about 21 per cent below that obtained by two successive precipitations without interval, which has been shown to remove all the ThX separable by the process. The rate of recovery of this twenty-three times precipitated hydroxide was then measured (Fig. 4). It will be seen that it is now quite normal, and the initial drop characteristic of the ordinary curve is quite absent. It is, in fact, almost identical with the ordinary curve (Fig. 1) that has been produced back to cut the vertical axis, and there is thus no doubt that there is a residual activity of thorium unconnected apparently with ThX, and constituting about one-fourth of the whole.

The decay curves of several of the fractions of ThX separated in this experiment after varying intervals of time were taken for the first few days. All of them showed the initial rise of about 15 per cent at the end of eighteen hours, and then a normal decay to zero. The position is thus proved that the initial irregularities are caused by the secondary radiation excited by ThX upon the surrounding matter. By suitably choosing the conditions the recovery curve can be made to rise normally from a constant minimum, and the decay curve be shown to consist of two curves—the first the rate of production of excited radio-activity, and the second the rate of decay of the activity as a whole. It is a significant fact that exactly similar curves have already been obtained by one of us (*Phys. Zeit.*, 1903, p. 254) for the excited radio-activity produced by the thorium emanation under very similar conditions. If a negatively charged wire be ex-

posed for a few minutes only to the thorium emanation, the excited radio-activity produced at first increases to several times its value for the first few hours after the exciting cause is removed, and then commences to decay, exactly as in the case of ThX.

So far nothing has been stated as to whether the excited radio-activity, which contributes about 21 per cent of the total activity of thorium, is the same or different from the known type produced by the thorium emanation. All that has been assumed is that it should follow the same general law, *i.e.*, the effect will increase with the time of action of the exciting cause, and decrease with time after the cause is removed. If the rate of rise of the excited activity be worked out from the curves given (Fig. 5), it will



be found to agree with that of the ordinary excited activity, *i.e.*, it rises to half value in about twelve hours. Curve 1 is the observed decay curve for ThX. Curve 2 is the theoretical curve, assuming that it decreases geometrically with the time, and falls to half value in four days. Curve 3 is obtained by plotting the difference between these two, and therefore constitutes the curve of excited activity. Curve 4 is the experimental curve obtained for the rise of the excited radio-activity from the thorium emanation when the exciting cause is constant. But the exciting cause (ThX) in the present case is not constant, but is itself falling to half value in four days, and hence the difference curve, at first almost on the other, drops away from it as time goes on, and finally decays to zero. Curve 3, Fig. 1, is a similar difference curve, representing the decay of excited activity, plotted from the recovery curve of thorium. There is thus no reason to doubt that the effect is the same as that produced by the thorium emanation, which is itself a secondary effect of ThX.

9. The Non-separable Radio-activity of Thorium.

It has not yet been found possible by any means to free thorium from its residual activity, and the place of this part in the scheme of radio-activity of thorium remains to be considered. Disregarding the view that it is a separate phenomenon and not connected with the major part of the activity, two hypotheses can be brought forward capable of experimental test, and, in accordance with the views advanced on the nature of radio-activity, to account for existence of this part. First, if there was a second type of excited activity produced by ThX, similar to that known, but with a very slow rate of decay, it would account for the existence of the non-separable activity. If this is true

it will not be found possible to free thorium from this activity by chemical means, but the continuous removal of ThX over a very long period would, as in the above case, cause its spontaneous decay.

Secondly, if the change which gives rise to ThX produces a second type of matter at the same time, *i.e.*, if it is of the type of a decomposition rather than a depolymerisation, the second type would also in all probability be radio-active, and would cause the residual activity. On this view the second type of matter should also be amenable to separation by chemical means, although it is certain from the failure of the methods already tried that it resembles thorium much more closely than ThX. But until it is separated from the thorium producing it, its activity will not decay spontaneously. Thus, what has already been shown to hold for ThX will be true for the second constituent if methods are found to remove it from the thorium.

It will be shown in a following communication by one of us that uranium also possesses a non separable radio-activity extremely analogous to that possessed by thorium, and whatever view is taken of the one will in all probability hold also for the other. This consideration makes the second hypothesis, that the residual activity is caused by a second non thorium type of matter produced in the original change, the more probable of the two.

(To be continued).

NOTE ON THE DETECTION OF ARSENIC AND SELENIUM IN SULPHUR.

By FRED. W. STEEL, F.C.S.

HAVING tried a number of methods* for the detection of arsenic and selenium in sulphur without getting satisfactory results, I devised the following one, by use of which very minute quantities of these elements can easily and with certainty be detected.

So far as I can learn from the literature at my disposal, which is fairly voluminous, the method detailed below has not been previously published. The procedure is as follows:—

Two hundred grms. of the finely-ground sample are placed in a cylinder of filter-paper in a 200 c.c. Soxhlet fat extractor, and extracted in the usual way by freshly-distilled pure carbon bisulphide. I allow about four hours—or longer—for this operation. When extraction is complete, the paper cylinder is withdrawn from the Soxhlet, and the carbon bisulphide with which it is soaked allowed to evaporate. The residue on the paper is then scraped into a No. 3 beaker, 50 c.c. strong nitric acid added, and the whole heated on the sand-bath (or, preferably, on the water-bath, if the results are not required immediately) until all nitric acid is driven off. One c.c. strong hydrochloric acid is next added; then, after a few minutes, about 5 c.c. warm water. The contents of beaker are well stirred, filtered through a small filter into a 7" × 1" test-tube, and the filter washed twice with the least possible quantity of water.

Now add to the contents of the test tube 20 c.c. strong hydrochloric acid, 1 or 2 c.c. of a fairly concentrated solution of stannous chloride in hydrochloric acid, and, lastly, 5 c.c. strong sulphuric acid. Warm gently, cover test-tube with a watch-glass, and allow to stand for some hours (preferably over night).

If arsenic—or selenium insoluble in carbon bisulphide (which I often find)—is present in the sulphur under examination, a dark brown precipitate settles down. The solution is filtered through a layer of asbestos (purified by boiling with aqua regia, washing, and igniting) on a

platinum filtering cone in an ordinary glass funnel, using the suction-pump.

The precipitate and asbestos are washed with cold water until perfectly free from acid, then removed from the platinum cone and dried at 100° C. When quite dry, they are transferred to a hard glass tube (about 7 m.m. bore) closed at one end; the tube is then drawn out, immediately above its contents, to about 1·5 m.m.; the narrow part being left about 80 m.m. long. The bulb portion, containing the asbestos, &c., is now heated to redness in a Bunsen flame. Arsenic and selenium, if present, are driven off and condense in the narrow part of the tube; the selenium generally appears in both the red and black modifications, and is at once identified by the characteristic odour which may be perceived at the open end of the tube, and which is an extremely delicate and unmistakable indication of its presence.

The part of the tube containing the sublimate is cut off and placed in a fresh ignition tube, similar to the first; this tube is drawn out in exactly the same manner, leaving a fair sized bulb, so that the arsenic and selenium may be oxidised as completely as possible on heating.*

The bulb of the ignition tube is now gradually heated, holding the tube horizontally; the arsenic and selenium are oxidised and volatilised, the oxides and some unoxidised selenium condensing in the narrow part of the tube.

The arsenious oxide forms a ring of beautiful glistening crystals, which can be identified with ease with a moderate microscopic power.

The selenium dioxide—in the entire absence of water—forms fern-shaped crystals. There is, however, nearly always a trace of water present, and therefore a solution of the oxide in minute globules is generally found in place of the crystals. In any case, it cannot be confounded with the arsenious oxide, the difference being very marked. The narrow part of the tube, containing the sublimate, is now sealed off, labelled, and kept for reference.

It is, of course, necessary to perform a blank test to ensure that the sulphuric, hydrochloric, and nitric acids used do not contain arsenic or selenium. In the case of the stannous chloride any precipitate which forms when the solution is prepared must be removed; the solution is then ready for use at any time.

If selenium has not been found associated with the arsenic, it will be necessary to distil off the carbon bisulphide from the extracted sulphur in the extraction flask; carefully break up the mass of sulphur, remove it from the flask, dry, and powder finely; return it to the flask, add about 200 c.c. strong (preferably pure, fuming) nitric acid, and digest in the water-bath for six hours, keeping a small funnel in flask neck to retard evaporation of nitric acid. The contents of the flask are now filtered through asbestos, the unoxidised sulphur washed twice with water, the filtrate then evaporated until copious white fumes of sulphuric acid appear; solution is poured (after cooling) into a 7" × 1" test-tube, 20 c.c. strong hydrochloric acid, then 1 or 2 c.c. of the stannous chloride solution mentioned above are added. Selenium, if present, is precipitated after standing, and may be identified by formation of the red sublimate in ignition tube, and also by odour on igniting.

Experiments are being undertaken to ascertain if the above method can be applied quantitatively.

Chemical Laboratory,
Cuming, Smith, and Co., Pty., Ltd.,
Yarraville, Melbourne, July 29, 1902.

Electro-chemical Equivalent of Silver.—A. Leduc.—The mass of silver deposited on the cathode by one coulomb usually depends on several circumstances. It seems, however, that it is possible to obtain a result accurate to one ten-thousandth in the determination of the electro-chemical equivalent of this metal by operating with a perfectly neutral or even basic bath at the beginning of the experiment, and so avoiding the formation of acid at the anode.—*Comptes Rendus*, cxxxv., No. 4.

* Arsenic appears to be more readily oxidised than selenium.

* In particular I may mention that of Schaeppi (*vide Crookes's "Select Methods in Chemical Analysis,"* Third Edition, p. 422), by which I have been quite unable to get anything approaching reliable results, owing to the fact that very dilute ammonium hydrate dissolves sulphur just as readily as it does arsenious sulphide.

OBITUARY.

SIR FREDERICK ABEL.

WE regret to announce the death of the distinguished chemist, Sir Frederick Abel, which occurred suddenly on Saturday night at his residence in Whitehall Court.

Frederick Augustus Abel was born in London on July 17, 1827, being the eldest son of J. L. Abel, of Woolwich, and grandson of A. C. A. Abel, Court miniature painter to the Grand Duke of Mecklenburg-Schwerin. Undeterred by warnings that it offered very slight prospects as a career, he determined to adopt chemistry as his profession, and was at once met by the difficulties which confronted every one of limited means, who, in the early years of Queen Victoria's reign, desired good scientific instruction at moderate expense. The Royal Polytechnic Institution was practically the only available place where the latter requirement was fulfilled, and, accordingly, in 1844, Abel's name was entered as a pupil on its books. But it was not long before he found that no attempt was made at methodical instruction; indeed, he soon began to doubt whether the "professor" had the ability to teach, even if he had had the wish. After spending six months in working through a standard textbook of chemistry according to his own devices, he decided that he had had enough of the Polytechnic Institution, and took his leave, the proud possessor of a testimonial setting forth the skill and minuteness with which his analyses had been conducted, and confidently recommending him to any post where a knowledge of practical chemistry might be required. But, luckily for him, a scheme for establishing in London a school of chemistry on the lines of Liebig's famous one at Giessen was successfully carried through about this time, and thus he was able to form one of the twenty-six students on the roll of the Royal College of Chemistry, when its temporary laboratory in George Street, Hanover Square, was opened in the autumn of 1845, under the direction of the famous German chemist, A. W. von Hofmann. At the college he spent some six years, during five of which he was one of Hofmann's assistants, and he only left to succeed Faraday as Professor of Chemistry at the Royal Military Academy. A few years later, in 1854, he was appointed Chemist to the War Office—a position which he filled for thirty-four years. His official duties naturally led him to devote attention to the study of explosives for military purposes, and thus he became intimately concerned in some of the most important developments that the latter part of last century witnessed in the manufacture and use of ammunition. Perhaps the most striking of these was the supersession of black powder by the so-called smokeless powders, and it may almost be said that Abel rendered this change possible. Of most of these powders, at any rate of the most successful ones, gun-cotton is a chief constituent. Now, though he was not the discoverer of gun-cotton, nor even the first to investigate its properties, he devised such improvements in the processes of preparation as to enable it to be safely manipulated and efficiently applied to practical uses. In Austria Baron von Lenk had endeavoured to produce the substance in a form which could be utilised in firearms, but his system of regulating the rapidity of burning by special arrangements of the threads achieved but indifferent success. In 1862 Austria communicated to the British Government the details of von Lenk's work, on the basis of which Abel was instructed, as the War Office chemist, to carry out experiments on the substance and inquire into its manufacture, constitution, stability, &c. His researches resulted in the elaboration of the system of preparation which has come into extensive use not only in this country but also in Germany, France, and elsewhere. After being nitrated, the cotton is reduced to pulp, as in the process of making paper. In this condition it can be more thoroughly washed than when in a fibrous

state, and thus can be completely freed from all traces of acid, the presence of which is so dangerous to its stability. When purified, the pulp is compressed by hydraulic power into homogeneous masses of any desired shape or size, and in this way control is gained over the rapidity of explosion, which is greatly modified according to the mechanical condition of the material. It is claimed that, when all the stipulated regulations are strictly observed, the preparation of gun-cotton, though it is a far stronger explosive, is much safer than that of ordinary black powder.

The possibility of utilising this substance for the production of smokeless powders had occurred to Abel, as to others, long before they became fashionable, but it was not until reports began to arrive of the wonderful results that were being attained with them by Continental nations that he received any official encouragement to pursue the subject. In 1888 the British Government had become alive to the situation, and appointed a special committee to examine the various kinds of smokeless powder then in existence, and to report which of them was best adapted to the requirements of the British Army and Navy. The problem was complicated by the fact that it was not so much the best powder absolutely that had to be selected as the powder best suited to the peculiarities of the Lee-Metford rifle. That weapon in its then form had an extraordinarily rapid twist in its rifling, and the difficulty was to get a powder such as would, with the charge available in the chamber, be able to overcome the resistance of the rifling and yet project the bullet with the desired muzzle velocity. The committee, of which Abel was president, spent some years in their inquiry, investigating every powder of which they could obtain samples and testing the properties of each by minute experiments. In the end they failed to find anyone the adoption of which they could unreservedly recommend. Compounds were brought to their notice which, with certain modifications, might have proved suitable, but, as their inventors declined to make the required changes, the idea of adopting any of them had to be abandoned. In these circumstances the committee set themselves to devise a powder which should be as free as possible from the defects noticed in the mixtures submitted to examination, and the result of their labours was that Sir Frederick Abel, in conjunction with Professor Dewar, patented the substance which is now the standard powder of the British services, and which is known as cordite, in allusion to the cord-like form in which it is prepared. All things considered, cordite, of which the main constituents are gun-cotton and nitroglycerin, may, perhaps, be described as the best smokeless powder in existence, and it would probably be still better at the present time if those responsible for its manufacture had paid more attention to suggestions made for its improvement by its original inventors; at any rate, that appreciation of its merits which is implied by extensive imitation has been accorded it abroad, while at home several inventors have paid it the compliment of attempting to prove it to be the precise material which their patent specifications were designed to cover.

In addition to his work on gun-cotton, Sir Frederick Abel, in conjunction with Sir Andrew Noble, carried out what is probably the most complete investigation into the processes attendant on the firing of black powder that has ever been attempted. Charges up to 20 lbs. were exploded in perfectly closed vessels, and the resulting products submitted to analysis. In this way the enormous influence of the size of the grains and of the pressure under which they were fired was made apparent. The experiments showed that any attempt to construct a general chemical expression for the metamorphosis of normal powder was of no practical value whatever, because the same powder fired under different pressures, and the same powder fired at the same pressure, but in different sized grains, gave quite different products. To the theory of detonation Abel made important contributions, his ingenious experiments throwing much light on the conditions of its occurrence

and the rapidity of its transmission. The latter, he showed, might, in the case of wet gun-cotton, rise as high as four miles a second. The construction of fuses—electrical and other—also engaged his attention, and his knowledge of blasting powders and methods of blasting was of great advantage to the Royal Commission on Accidents in Mines, of which he was appointed one of the scientific members at its constitution in 1879.

When mineral oils came into use as a means of domestic illumination it was soon found necessary to frame regulations for their storage, because some of the constituents of the mixture termed petroleum are so volatile that at ordinary temperatures it may give off inflammable vapours which in certain conditions become explosive. The first Petroleum Act, passed in 1862, defined as dangerous, and placed restrictions on the sale of any petroleum that gave off vapour at a lower temperature than 100° F., but as it omitted to specify any method of testing the oil, it was practically inoperative. During the next few years Sir Frederick Abel and other chemists investigated the matter, and as a result, in 1868, the second Petroleum Act was passed, legalising the Abel "open-test" apparatus. In time it was recognised not only that the indications of this instrument were inherently untrustworthy, but that it lent itself to manipulation on the part of an operator who had some motive for not discovering the truth. In 1875, therefore, the whole question was referred to Sir Frederick Abel. He reported that, though the established flashing-point of 100° was calculated to afford adequate protection to the public, the method by which it was ascertained was not satisfactory, and at the same time, as an improvement, he brought forward the Abel "close-test" instrument. This was legalised in 1879, and has been the British standard ever since, besides being adopted, with or without modification, by several other countries. The flash-point of a given oil as determined by the new apparatus not being the same as that shown by the old one, it became necessary to fix the relations between the two. To this end a thousand samples of oil were tested by both methods, and it was found that on the average the temperature at which the oil vapour flashed was 27° lower with the close than with the open test. Hence, the flash-point of 73° was adopted as the equivalent of the 100° prescribed under the old system, and has been adhered to ever since. Agitations (it is to be feared not always inspired by pure regard for the public safety) have from time to time been started to effect an alteration, but without success. The first condition for reducing the annual tale of accidents would rather appear to be due attention to common-sense principles of lamp construction and management, such as are embodied in Sir Frederick Abel's reports to the Metropolitan Board of Works and the Chief Inspector of Explosives.

In 1885 Sir Frederick Abel rendered valuable service as a member of the Council of the Inventions Exhibition, and on the formation of the Imperial Institute, two years later, he was appointed organising secretary and general director. The duties of this office he continued to perform, in later years receiving no pecuniary reward for his services, until the end of his life, and practically until the end of the existence of the Imperial Institute as an independent entity; for it was only in July last that the Royal Assent was given to an Act, which will probably become operative at the beginning of next year, for the transference of the Institute to the control of the Board of Trade. The tenure of this arduous and difficult position did not prevent him from undertaking a great deal of other scientific and official work. He ceased to be Chemist to the War Office in 1888, but immense labour was involved in the investigations of the Special Committee on Explosives, which lasted till 1891. As a prominent member of the Goldsmiths' Company he took considerable interest in the subjects of technical education and original research, and was instrumental in establishing

at the Imperial Institute well-equipped research laboratories in connection with its scientific and technical department.

Sir Frederick Abel received recognition of his scientific work from many quarters. Elected a Fellow of the Royal Society in 1860, he was awarded a Royal medal by that body in 1887. At various times he served as President of the British Association, the Chemical Society, the Institute of Chemistry, the Society of Chemical Industry, and the Institution of Electrical Engineers. Of the Iron and Steel Institute he was elected President in 1891, as a recognition of his scientific contributions to the chemistry of iron and steel, and he was awarded its Bessemer medal in 1897. The University of Cambridge, in which he filled the office of Rede Lecturer, conferred the honorary degree of D.Sc. on him in 1888, and Oxford that of D.C.L. in 1883. He was made C.B. in 1877, a knight in 1883, K.C.B. in 1891, a baronet in 1893, and G.C.V.O. in 1901.

He was twice married, first to Sarah, daughter of Mr. James Blanch, of Bristol, and secondly to Giulietta de la Feuillade, but he has left no heir to the baronetcy.—*The Times*, September 8, 1902.

NOTICES OF BOOKS.

Chemicals and Allied Products. Census Bulletin. By C. E. MUNROE and T. M. CHATARD. Washington. 1902.

THIS volume of statistics is issued in connection with the twelfth census of the United States, and provides a complete account of the present state of chemical industries in the country. Some differences have been made from the reports of 1890 to eliminate certain defects, but care has been taken to preserve the basis of comparison with previous censuses. A short description of methods and processes is attached to the tables of statistics referring to each group of products, and in cases of innovations of importance these descriptive portions are fairly complete; for instance, the contact method for the preparation of sulphuric acid receives special attention, and Knietech's paper on the subject, which recently appeared in the *Berichte der Deutschen Gesellschaft*, is abstracted. Considerable space is devoted to electro-chemistry, a branch of the science which has not been included in any previous census, as it has practically sprung into existence within the last ten years. A useful digest of United States patents relating to chemical industries (products and processes) is added.

Die Gewinnung des Aluminiums und dessen Bedeutung für Handel und Industrie. ("The Preparation of Aluminium and its Commercial and Industrial Importance"). By ADOLPHE MINET. Halle-a-S.: William Knapp. 1902.

THIS volume is the second of a series of monographs on applied electro-chemistry; in it are described the most recent developments in processes for the preparation of aluminium, and it is well illustrated. Purely chemical methods are not neglected, and no modifications of detail are allowed to pass unnoticed. A full account of Minet's process, which is employed on a large scale, is given, and is specially interesting in view of the fact that there is some difficulty in obtaining trustworthy descriptions of technical processes. The uses to which aluminium may be put are also discussed in the volume, and the characters and properties of the most important alloys. The text has been rendered into German by Dr. Emil Abel, of Vienna. This work must be accorded praise as a careful compilation; it will, no doubt, be found of considerable value by experts.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 4, July 28, 1902.

Reduction of Nitrogen Derivatives by the Method of Direct Hydrogenation in Contact with Finely-divided Metals.—Paul Sabatier and J. B. Senderens.—In a former paper the authors described a general method of direct hydrogenation which can be used in many cases to transform organic nitrogen derivatives into the corresponding amine derivatives. Nitrobenzene, nitrotoluenes, and nitronaphthalenes are thus regularly changed into aniline, toluidine, and naphthylamine. They now extend the application of this reaction to the analogous case of nitronaphthalene and the formenic nitrogen derivatives, nitromethane and nitroethane.

Precipitation of Chlorides and Bromides of Cadmium, Mercury, and Tin by means of Sulphuric Acid.—Georges Viard.—An excess of concentrated sulphuric acid precipitates from their solutions the chlorides and bromides of cadmium, mercury, and tin. These salts can be recognised by the reaction described by the author in a previous paper (*Comptes Rendus*, July 21, 1902). The mixture of copper sulphate with a large excess of sulphuric acid, which usually gives a yellow precipitate with chlorides and a black one with bromides, only gives white precipitates with chlorides and bromides of cadmium, mercury, and tin.

MISCELLANEOUS.

Schools of Chemistry, &c.—The following additional information of interest to Students has been received:—

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming public and technical analysts and chemical advisers on scientific subjects; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University approved by the Council, or in the laboratory of a Fellow of the Institute, with the object of adopting the profession of Analytical and Consulting Chemistry. *The Intermediate Examination.*—Candidates for admission to the Intermediate Examination are required to produce evidence (I) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Advanced Mathematics; (ii.) Mechanics and Chemical Engineering; (iii.) Metallurgy; (iv.) Geology and Mineralogy; (v.) Physiology; (vi.) Bacteriology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' training in a recognised Institution as indicated above, and work systematically for two other years in the laboratory of a Fellow of the Institute. A

Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also passed in at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.).*—Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C.).*—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained on application to Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C. Price One Shilling.

UNIVERSITY OF BIRMINGHAM.—*Metallurgy*: Professor, Thomas Turner, M.Sc., A.R.S.M., F.I.C. Three courses of Lectures are given during the year—

- (a) Sixty lectures on the Principles and Practice of Metallurgy. Fee, £3 3s.
- (b) Thirty lectures for Senior Metallurgical Students. Fee, £1 11s. 6d.
- (c) A Special Course of Metallurgical Lectures and Laboratory Work for Engineering Students. Fee, £4 4s.

A course of Lectures and Laboratory Work on Determinative Mineralogy will also be given. Fee, £3 3s. Pending the completion of the new Metallurgical Laboratories and Workshops now in course of erection on the Burnbrook site, practical instruction will be conducted in the laboratories of the Municipal Technical School, which have been specially designed and fully equipped for all forms of metallurgical instruction.

BATTERSEA POLYTECHNIC.—Principal, Mr. S. H. Wells, A.M.I.C.E., A.M.I.M.E. Chemical Department: Head of Department, Mr. John Wilson, M.Sc.; Assistant Lecturers and Demonstrators, J. L. White, M.Sc., H. G. Wayling, B.Sc., J. Hart-Smith, A.R.C.S., A.I.C., and B. C. Polkinghorne, B.Sc., F.C.S. Lecturer in Paper Testing, E. J. Stallybrass. Lecturer in Paper Making, J. Clayton Beadle, F.I.C., F.C.S. Lecturer in Gas Manufacture, J. G. Taplay. Steward and Lecture Assistant, A. E. Dawe. The Chemical Department provides complete courses of instruction in Inorganic and Organic Chemistry, Theoretical and Practical, the courses extending over four years for Evening Students, three years for Day Students, in preparation for the London B.Sc. and various professional examinations. Special courses are also given in Gas Analysis, Gas Manufacture, Paper and Pulp Testing, Paper Making, Assaying, Saccharimetry, Oils, Fats, Soaps, and Candles, Chemistry of Foods, Fuel Analysis, &c. The Senior Day Department provides complete courses of instruction for intending works chemists and general analysts. Students can be admitted for Research and other special work. Recent additions to the equipment comprise an accurate gas analysis machine for research purposes and a small electric furnace.

EAST LONDON TECHNICAL COLLEGE,
MILE END ROAD, E.

A Special Course of Lectures on ELECTRO-CHEMISTRY, dealing with the most recent developments of the subject, will be delivered by Professor R. A. LEHFELDT, D.Sc., on THURSDAY EVENINGS at 8.45 p.m. Students will have the opportunity of doing Practical Work on Thursdays from 7 to 8.45 p.m. The fee for the Course, which extends from September 25th to March 26th, is 15s.

THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2234.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BELFAST, 1902.

INAUGURAL ADDRESS OF THE PRESIDENT,
PROF. JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

(Continued from p. 132).

History of Cold and the Absolute Zero.

It was Tyndall's good fortune to appear before you at a moment when a fruitful and comprehensive idea was vivifying the whole domain of scientific thought. At the present time no such broad generalisation presents itself for discussion, while, on the other hand, the number of specialised studies has enormously increased. Science is advancing in so broad a front by the efforts of so great an army of workers that it would be idle to attempt within the limits of an address to the most indulgent of audiences anything like a survey of chemistry alone. But I have thought it might be instructive, and perhaps not uninteresting, to trace briefly in broad outline the development of that branch of study with which my own labours have been recently more intimately connected—a study which I trust I am not too partial in thinking is as full of philosophical interest as of experimental difficulty. The nature of heat and cold must have engaged thinking men from the very earliest dawn of speculation upon the external world; but it will suffice for the present purpose if, disregarding ancient philosophers and even medieval alchemists, we take up the subject where it stood after the great revival of learning, and as it was regarded by the father of the inductive method. That this was an especially attractive subject to Bacon is evident from the frequency with which he recurs to it in his different works, always with lamentation over the inadequacy of the means at disposal for obtaining a considerable degree of cold. Thus in the chapter in the *Natural History*, "*Sylva Sylvarum*," entitled "Experiments in consort touching the Production of Cold," he says, "The production of cold is a thing very worthy of the inquisition both for the use and the disclosure of causes. For heat and cold are nature's two hands whereby she chiefly worketh, and heat we have in readiness in respect of the fire, but for cold we must stay till it cometh or seek it in deep caves or high mountains, and when all is done we cannot obtain it in any great degree, for furnaces of fire are far hotter than a summer sun, but vaults and hills are not much colder than a winter's frost." The great Robert Boyle was the first experimentalist who followed up Bacon's suggestions. In 1682 Boyle read a paper to the Royal Society on "New Experiments and Observations touching Cold, or an Experimental History of Cold," published two years later in a separate work. This is really a most complete history of everything known about cold up to that date, but its great merit is the inclusion of numerous experiments made by Boyle himself on frigorific mixtures, and the general effects of such upon matter. The agency chiefly used by Boyle in the conduct of his experiments was the glaciating mixture of snow or ice and salt. In the course of his experiments he made many important observations. Thus he observed that the salts which did not help the snow or ice to dissolve faster gave no effective freezing. He showed that water in becoming ice expands by about one ninth of its volume, and bursts gun-barrels. He attempted to counteract the ex-

pansion and prevent freezing by completely filling a strong iron ball with water before cooling; anticipating that it might burst the bottle by the stupendous force of expansion, or that if it did not, then the ice produced might under the circumstances be heavier than water. He speculated in an ingenious way on the change of water into ice. Thus he says, "If cold be but a privation of heat through the recess of that ethereal substance which agitated the little eel-like particles of the water and thereby made them compose a fluid body, it may easily be conceived that they should remain rigid in the postures in which the ethereal substance quitted them, and thereby compose an unfluid body like ice; yet how these little eels should by that recess acquire as strong an endeavour outwards as if they were so many little springs and expand themselves with so stupendous a force, is that which does not so readily appear." The greatest degree of adventitious cold Boyle was able to produce did not make air exposed to its action lose a full tenth of its own volume, so that, in his own words, the cold does not "weaken the spring by anything near so considerable as one would expect." After making this remarkable observation and commenting upon its unexpected nature, it is strange Boyle did not follow it up. He questions the existence of a body of its own nature supremely cold, by participating in which all other bodies obtain that quality, although the doctrine of a *primum frigidum* had been accepted by many sects of philosophers; for, as he says, "if a body being cold signify no more than its not having its sensible parts so much agitated as those of our sensorium, it suffices that the sun or the fire or some other agent, whatever it were, that agitated more vehemently its parts before, does either now cease to agitate them, or agitates them but very remissly, so that till it be determined whether cold be a positive quality or but a privative it will be needless to contend what particular body ought to be esteemed the *primum frigidum*." The whole elaborate investigation cost Boyle immense labour, and he confesses that he "never handled any part of natural philosophy that was so troublesome and full of hardships." He looked upon his results but as a "beginning" in this field of inquiry, and for all the trouble and patience expended he consoled himself with the thought of "men being oftentimes obliged to suffer as much wet and cold and dive as deep to fetch up sponges as to fetch up pearls." After the masterly essay of Boyle, the attention of investigators was chiefly directed to improving thermometrical instruments. The old air thermometer of Galileo being inconvenient to use, the introduction of fluid thermometers greatly aided the inquiry into the action of heat and cold. For a time great difficulty was encountered in selecting proper fixed points on the scales of such instruments, and this stimulated men like Huygens, Newton, Hooke, and Amontons to suggest remedies and to conduct experiments. By the beginning of the eighteenth century the freezing-point and the boiling-point of water were agreed upon as fixed points, and the only apparent difficulties to be overcome were the selection of the fluid, accurate calibration of the capillary tube of the thermometer, and a general understanding as to scale divisions. It must be confessed that great confusion and inaccuracy in temperature observations arose from the variety and crudeness of the instruments. This led Amontons in 1702-3 to contribute two papers to the French Academy which reveal great originality in the handling of the subject, and which, strange to say, are not generally known. The first discourse deals with some new properties of the air and the means of accurately ascertaining the temperature in any climate. He regarded heat as due to a movement of the particles of bodies, though he did not in any way specify the nature of the motion involved; and as the general cause of all terrestrial motion, so that in its absence the earth would be without movement in its smallest parts. The new facts he records are observations on the spring or pressure of air brought about by the action of heat. He

shows that different masses of air measured at the same initial spring or pressure, when heated to the boiling-point of water, acquire equal increments of spring or pressure, provided the volume of the gas be kept at its initial value. Further, he proves that if the pressure of the gas before heating be doubled or tripled, then the additional spring or pressure resulting from heating to the boiling-point of water is equally doubled or tripled. In other words, the ratio of the total spring of air at two definite and steady temperatures and at constant volume is a constant, independent of the mass or the initial pressure of the air in the thermometer. These results led to the increased perfection of the air thermometer as a standard instrument, Amontons' idea being to express the temperature at any locality in fractions of the degree of heat of boiling water. The great novelty of the instrument is that temperature is defined by the measurement of the length of a column of mercury. In passing, he remarks that we do not know the extreme of heat and cold, but that he has given the results of experiments which establish correspondences for those who wish to consider the subject. In the following year Amontons contributed to the Academy a further paper extending the scope of the inquiry. He there pointed out more explicitly that as the degrees of heat in his thermometer are registered by the height of a column of mercury, which the heat is able to sustain by the spring of the air, it follows that the extreme cold of the thermometer will be that which reduces the air to have no power of spring. This, he says, will be a much greater cold than what we call "very cold," because experiments have shown that if the spring of the air at boiling-point is 73 inches, the degree of heat which remains in the air when brought to the freezing-point of water is still very great, for it can still maintain the spring of 51½ inches. The greatest climatic cold on the scale of units adopted by Amontons is marked 50, and the greatest summer heat 58, the value for boiling water being 73, and the zero being 52 units below the freezing-point. Thus Amontons was the first to recognise that the use of air as a thermometric substance led to the inference of the existence of a zero of temperature, and his scale is nothing else than the absolute one we are now so familiar with. It results from Amontons' experiments that the air would have no spring left if it were cooled below the freezing-point of water to about 2½ times the temperature range which separates the boiling-point and the freezing-point. In other words, if we adopt the usual centennial difference between these two points of temperature as 100 degrees, then the zero of Amontons' air thermometer is *minus* 240 degrees. This is a remarkable approximation to our modern value for the same point of *minus* 273 degrees. It has to be confessed that Amontons' valuable contributions to knowledge met with that fate which has so often for a time overtaken the work of too-advanced discoverers; in other words, it was simply ignored, or in any case not appreciated by the scientific world either of that time or half a century later. It is not till Lambert, in his work on "Pyrometrie" published in 1779, repeated Amontons' experiments and endorsed his results that we find any further reference to the absolute scale or the zero of temperature. Lambert's observations were made with the greatest care and refinement, and resulted in correcting the value of the zero of the air scale to *minus* 270 degrees as compared with Amontons' *minus* 240 degrees. Lambert points out that the degree of temperature which is equal to zero is what one may call absolute cold, and that at this temperature the volume of the air would be practically nothing. In other words, the particles of the air would fall together and touch each other, and become dense like water; and from this it may be inferred that the gaseous condition is caused by heat. Lambert says that Amontons' discoveries had found few adherents because they were too beautiful and advanced for the time in which he lived.

About this time a remarkable observation was made by Professor Braun at Moscow, who, during the severe winter

of 1759, succeeded in freezing mercury by the use of a mixture of snow and nitric acid. When we remember that mercury was regarded as quite a peculiar substance possessed of the essential quality of fluidity, we can easily understand the universal interest created by the experiment of Braun. This was accentuated by the observations he made on the temperature given by the mercury thermometer, which appeared to record a temperature as low as *minus* 200° C. The experiments were soon repeated by Hutchins at Hudson's Bay, who conducted his work with the aid of suggestions given him by Cavendish and Black. The result of the new observations was to show that the freezing-point of mercury is only *minus* 40° C., the errors in former experiments having been due to the great contraction of the mercury in the thermometer in passing into the solid state. From this it followed that the enormous natural and artificial colds which had generally been believed in had no proved existence. Still the possible existence of a zero of temperature very different from that deduced from gas thermometry had the support of such distinguished names as those of Laplace and Lavoisier. In their great memoir on "Heat," after making what they consider reasonable hypotheses as to the relation between specific heat and total heat, they calculate values for the zero which range from 1500° to 3000° below melting ice. On the whole, they regard the absolute zero as being in any case 600° below the freezing-point. Lavoisier, in his "Elements of Chemistry" published in 1792, goes further in the direction of indefinitely lowering the zero of temperature when he says, "We are still very far from being able to produce the degree of absolute cold, or total deprivation of heat, being unacquainted with any degree of coldness which we cannot suppose capable of still further augmentation: hence it follows we are incapable of causing the ultimate particles of bodies to approach each other as near as possible, and thus these particles do not touch each other in any state hitherto known." Even as late as the beginning of the nineteenth century we find Dalton, in his new system of "Chemical Philosophy," giving ten calculations of this value, and adopting finally as the natural zero of temperature *minus* 3000° C.

In Black's lectures we find that he takes a very cautious view with regard to the zero of temperature, but as usual is admirably clear with regard to its exposition. Thus he says, "We are ignorant of the lowest possible degree or beginning of heat. Some ingenious attempts have been made to estimate what it may be, but they have not proved satisfactory. Our knowledge of the degrees of heat may be compared to what we should have of a chain, the two ends of which were hidden from us, and the middle only exposed to our view. We might put distinct marks on some of the links, and number the rest according as they are nearest to or further removed from the principal links; but not knowing the distance of any links from the end of the chain we could not compare them together with respect to their distance, or say that one link was twice as far from the end of the chain as another." It is interesting to observe, however, that Black was evidently well acquainted with the work of Amontons, and strongly supports his inference as to the nature of air. Thus, in discussing the general cause of vaporisation, Black says that some philosophers have adopted the view "that every palpable elastic fluid in nature is produced and preserved in this form by the action of heat. Mr. Amontons, an ingenious member of the late Royal Academy of Sciences, at Paris, was the first who proposed this idea with respect to the atmosphere. He supposed that it might be deprived of the whole of its elasticity and condensed, and even frozen into a solid matter were it in our power to apply to it a sufficient cold; that it is a substance that differs from others by being incomparably more volatile, and which is therefore converted into vapour and preserved in that form by a weaker heat than any that ever happened or can obtain in this globe, and which therefore cannot appear under any other form than

the one it now wears, so long as the constitution of the world remains the same as at present." The views that Black attributes to Amontons have been generally associated with the name of Lavoisier, who practically admitted similar possibilities as to the nature of air; but it is not likely that in such matters Black would commit any mistake as to the real author of a particular idea, especially in his own department of knowledge. Black's own special contribution to low-temperature studies was his explanation of the interaction of mixtures of ice with salts and acids by applying the doctrine of the latent heat of fluidity of ice to account for the frigorific effect. In a similar way Black explained the origin of the cold produced in Cullen's remarkable experiment of the evaporation of ether under the receiver of an air-pump by pointing out that the latent heat of vaporisation in this case necessitated such a result. Thus, by applying his own discoveries of latent heat, Black gave an intelligent explanation of the cause of all the low-temperature phenomena known in his day.

After the gaseous laws had been definitely formulated by Gay-Lussac and Dalton, the question of the absolute zero of temperature, as deduced from the properties of gases, was revived by Clement and Desormes. These distinguished investigators presented a paper on the subject to the French Academy in 1812, which, it appears, was rejected by that body. The authors subsequently elected to publish it in 1819. Relying on what we know now to have been a faulty hypothesis, they deduced from observations on the heating of air rushing into a vacuum the temperature of *minus* 267 degrees as that of the absolute zero. They further endeavoured to show, by extending to lower temperatures the volume or the pressure coefficients of gases given by Gay-Lussac, that at the same temperature of *minus* 267 degrees the gases would contract so as to possess no appreciable volume, or, alternatively, if the pressure was under consideration, it would become so small as to be non-existent. Although full reference is given to previous work bearing on the same subject, yet, curiously enough, no mention is made of the name of Amontons. It certainly gave remarkable support to Amontons' notion of the zero to find that simple gases like hydrogen and compound gases like ammonia, hydrochloric, carbonic, and sulphurous acids should all point to substantially the same value for this temperature. But the most curious fact about this research of Clement and Desormes is that Gay-Lussac was a bitter opponent of the validity of the inferences they drew either from his work or their own. The mode in which Gay-Lussac regarded the subject may be succinctly put as follows:—A quick compression of air to one-fifth volume raises its temperature to 300 degrees, and if this could be made much greater and instantaneous the temperature might rise to 1000 or 2000 degrees. Conversely, if air under five atmospheres were suddenly dilated, it would absorb as much heat as it had evolved during compression, and its temperature would be lowered by 300 degrees. Therefore, if air were taken and compressed to fifty atmospheres or more, the cold produced by its sudden expansion would have no limit. In order to meet this position Clement and Desormes adopted the following reasoning:—They pointed out that it had not been proved that Gay-Lussac was correct in his hypothesis, but that in any case it tacitly involves the assumption that a limited quantity of matter possesses an unlimited supply of heat. If this were the case, then heat would be unlike any other measurable thing or quality. It is, therefore, more consistent with the course of nature to suppose that the amount of heat in a body is like the quantity of elastic fluid filling a vessel, which, while definite in original amount, one may make less and less by getting nearer to a complete exhaustion. Further, to realise the absolute zero in the one case is just as impossible as to realise the absolute vacuum in the other; and as we do not doubt a zero of pressure, although it is unattainable, for the same reason we ought to accept the

reality of the absolute zero. We know now that Gay-Lussac was wrong in supposing the increment of temperature arising from a given gaseous compression would produce a corresponding decrement from an identical expansion. After this time the zero of temperature was generally recognised as a fixed ideal point, but in order to show that it was hypothetical a distinction was drawn between the use of the expressions, zero of absolute temperature and the absolute zero.

The whole question took an entirely new form when Lord Kelvin, in 1848, after the mechanical equivalent of heat had been determined by Joule, drew attention to the great principles underlying Carnot's work on the "Motive Power of Heat," and applied them to an absolute method of temperature measurement, which is completely independent of the properties of any particular substance. The principle was that for a difference of one degree on this scale, between the temperatures of the source and refrigerator, a perfect engine should give the same amount of work in every part of the scale. Taking the same fixed points as for the centigrade scale, and making 100 of the new degrees cover that range, it was found that the degrees not only within that range, but as far beyond as experimental data supplied the means of comparison, differed by only minute quantities from those of Regnault's air thermometer. The zero of the new scale had to be determined by the consideration that when the refrigerator was at the zero of temperature the perfect engine should give an amount of work equal to the full mechanical equivalent of the heat taken up. This led to a zero of 273 degrees below the temperature of freezing water, substantially the same as that deduced from a study of the gaseous state. It was a great advance to demonstrate by the application of the laws of thermodynamics not only that the zero of temperature is a reality, but that it must be located at 273 degrees below the freezing-point of water. As no one has attempted to impugn the solid foundation of theory and experiment on which Lord Kelvin based his thermodynamic scale, the existence of a definite zero of temperature must be acknowledged as a fundamental scientific fact.

Liquefaction of Gases and Continuity of State.

In these speculations, however, chemists were dealing theoretically with temperatures to which they could not make any but the most distant experimental approach. Cullen, the teacher of Black, had indeed shown how to lower temperature by the evaporation of volatile bodies, such as ether, by the aid of the air-pump, and the later experiments of Leslie and Wollaston extended the same principle. Davy and Faraday made the most of the means at command in liquefying the more condensable gases, while at the same time Davy pointed out that they in turn might be utilised to procure greater cold by their rapid re-conversion into the ætiform state. Still the chemist was sorely hampered by the want of some powerful and accessible agent for the production of temperatures much lower than had ever been attained. That want was supplied by Thilorier, who in 1835 produced liquid carbonic acid in large quantities, and further made the fortunate discovery that the liquid could be frozen into a snow by its own evaporation. Faraday was prompt to take advantage of this new and potent agent. Under exhaustion he lowered its boiling-point from *minus* 78° C. to *minus* 110° C., and by combining this low temperature with pressure all the gases were liquefied by the year 1844, with the exception of the three elementary gases—hydrogen, nitrogen, and oxygen, and three compound gases—carbonic oxide, marsh gas, and nitric oxide; Andrews some twenty-five years after the work of Faraday attempted to induce change of state in the uncondensed gases by using much higher pressures than Faraday employed. Combining the temperature of a solid carbonic acid bath with pressures of 300 atmospheres, Andrews found that none of these gases exhibited any appearance of liquefaction in such high states of condensation; but so

far as change of volume by high compression went, Andrews confirmed the earlier work of Natterer by showing that the gases become proportionately less compressible with growing pressure. While such investigations were proceeding, Regnault and Magnus had completed their refined investigations on the laws of Boyle and Gay-Lussac. A very important series of experiments was made by Joule and Kelvin "On the Thermal Effects of Fluids in Motion" about 1862, in which the thermometrical effects of passing gases under compression through porous plugs furnished important data for the study of the mutual action of the gas molecules. No one, however, had attempted to make a complete study of a liquefiable gas throughout wide ranges of temperature. This was accomplished by Andrews in 1869, and his Bakerian Lecture "On the Continuity of the Gaseous and Liquid States of Matter," will always be regarded as an epoch-making investigation. During the course of this research Andrews observed that liquid carbonic acid raised to a temperature of 31°C . lost the sharp concave surface of demarcation between the liquid and the gas, the space being now occupied by a homogeneous fluid which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ, due to great local alterations of density. At temperatures above 31°C . the separation into two distinct kinds of matter could not be effected even when the pressure reached 400 atmospheres. This limiting temperature of the change of state from gas to liquid Andrews called the critical temperature. He showed that this temperature is constant, and differs with each substance, and that it is always associated with a definite pressure peculiar to each body. Thus the two constants, critical temperature and pressure, which have been of the greatest importance in subsequent investigations, came to be defined, and a complete experimental proof was given that "the gaseous and liquid states are only distinct stages of the same condition of matter, and are capable of passing into one another by a process of continuous change."

¶ In 1873 an essay "On the Continuity of the Gaseous and Liquid State," full of new and suggestive ideas, was published by van der Waals, who, recognising the value of Clausius's new conception of the virial in dynamics, for a long-continued series of motions, either oscillatory or changing exceedingly slowly with time, applied it to the consideration of the molecular movements of the particles of the gaseous substance, and after much refined investigation, and the fullest experimental calculation available at the time, devised his well-known equation of continuity. Its paramount merit is that it is based entirely on a mechanical foundation, and is in no sense empiric; we may therefore look upon it as having a secure foundation in fact, but as being capable of extension and improvement. James Thomson, realising that the straight-line breach of continuous curvature in the Andrews isothermals was untenable to the physical mind, propounded his emendation of the Andrews curves—namely, that they were continuous and of S form. We also owe to James Thomson the conception and execution of a three-dimensional model of Andrews' results, which has been of the greatest service in exhibiting the three variables by means of a specific surface afterwards greatly extended and developed by Professor Willard Gibbs. The suggestive work of James Thomson undoubtedly was a valuable aid to van der Waals, for as soon as he reached the point where his equation had to show the continuity of the two states this was the first difficulty he had to encounter, and he succeeded in giving the explanation. He also gave a satisfactory reason for the existence of a minimum value of the product of volume and pressure in the Regnault isothermals. His isothermals, with James Thomson's completion of them, were now shown to be the results of the laws of dynamics. Andrews applied the new equation to the consideration of the coefficients of expansion with temperature and of pressure with tem-

perature, showing that although they were nearly equal, nevertheless they were almost independent quantities. His investigation of the capillarity constant was masterly, and he added further to our knowledge of the magnitudes of the molecules of gases and of their mean free paths. Following up the experiments of Joule and Kelvin, he showed how their cooling coefficients could be deduced, and proved that they vanished at a temperature in each case which is a constant multiple of the specific critical temperature. The equation of continuity developed by van der Waals involved the use of three constants instead of one, as in the old law of Boyle and Charles, the latter being only utilised to express the relation of temperature, pressure, and volume, when the gas is far removed from its point of liquefaction. Of the two new constants one represents the molecular pressure arising from the attraction between the molecules, the other four times the volume of the molecules. Given these constants of a gas, van der Waals showed that his equation not only fitted into the general characters of the isothermals, but also gave the values of the critical temperature, the critical pressure, and the critical volume. In the case of carbonic acid the theoretical results were found to be in remarkable agreement with the experimental values of Andrews. This gave chemists the means of ascertaining the critical constants, provided sufficiently accurate data derived from the study of a few properly distributed isothermals of the gaseous substance were available. Such important data came into the possession of chemists when Amagat published his valuable paper on "The Isothermals of Hydrogen, Nitrogen, Oxygen, Ethylene, &c.," in the year 1880. It now became possible to calculate the critical data with comparative accuracy for the so-called permanent gases oxygen and nitrogen, and this was done by Sarrau in 1882. In the meantime a great impulse had been given to a further attack upon the so-called permanent gases by the suggestive experiments made by Pictet and Cailletet. The static liquefaction of oxygen was effected by Wroblewski in 1883, and thereby the theoretical conclusions derived from van der Waals' equation were substantially confirmed. The liquefaction of oxygen and air was achieved through the use of liquid ethylene as a cooling agent, which enabled a temperature of minus 140 degrees to be maintained by its steady evaporation *in vacuo*. From this time liquid oxygen and air came to be regarded as the potential cooling agents for future research, commanding as they did a temperature of 200 degrees below melting ice. The theoretical side of the question received at the hands of van der Waals a second contribution, which was even more important than his original essay, and that was his novel and ingenious development of what he calls "The Theory of Corresponding States." He defined the corresponding states of two substances as those in which the ratios of the temperature, pressure, and volume to the critical temperature, pressure, and volume respectively were the same for the two substances, and in corresponding states he showed that the three pairs of ratios all coincided. From this a series of remarkable propositions were developed, some new, some proving previous laws that were hitherto only empiric, and some completing and correcting faulty though approximate laws. As examples, he succeeded in calculating the boiling-point of carbonic acid from observations on ether vapour, proved Kopp's law of molecular volumes, and showed that at corresponding temperatures the molecular latent heats of vaporisation are proportional to the absolute critical temperature, and that under the same conditions the coefficients of liquid expansion are inversely proportional to the absolute critical temperature, and that the coefficients of liquid compressibility are inversely proportional to the critical pressure. All these propositions and deductions are in the main correct, though further experimental investigation has shown minor discrepancies requiring explanation. Various proposals have been made to supplement van der Waals' equation so as to bring it into line with experiments, some

being entirely empiric, others theoretical. Clausius, Sarrau, Wroblewski, Batteli, and others attacked the question empirically, and in the main preserved the co-volume (depending on the total volume of the molecules) unaltered while trying to modify the constant of molecular attraction. Their success depended entirely on the fact that, instead of limiting the number of constants to three, some of them have increased them to as many as ten. On the other hand, a series of very remarkable theoretical investigations has been made by van der Waals himself, by Kammerlingh Onnes, Korteweg, Jaeger, Boltzmann, Dieterici, and Riengam, and others, all directed in the main towards an admitted variation in the value of the co-volume while preserving the molecular attraction constant. The theoretical deductions of Tait lead to the conclusion that a substance below its critical point ought to have two different equations of the van der Waals type, one referring to the liquid, and the other to the gaseous phase. One important fact was soon elicited—namely, that the law of correspondence demanded only that the equation should contain not more than three constants for each body. The simplest extension is that made by Riengam, in which he increased the pressure for a given mean kinetic energy of the particles inversely in the ratio of the diminution of free volume, due to the molecules possessing linear extension. Berthelot has shown how a "reduced" isothermal may be got by taking two other prominent points as units of measurement instead of the critical coordinates. The most suggestive advance in the improvement of the van der Waals equation has been made by a lady, Mdme. Christine Meyer. The idea at the base of this new development may be understood from the following general statement:—van der Waals brings the van der Waals surfaces for all substances into coincidence at the point where volume, pressure, and temperature are nothing, and then stretches or compresses all the surfaces parallel to the three axes of volume, pressure, and temperature, until their critical points coincide. But on this plan the surfaces do not quite coincide, because the points where the three variables are respectively nothing are not corresponding points. Mdme. Meyer's plan is to bring all the critical points first into coincidence, and then to compress or extend all the representative surfaces parallel to the three axes of volume, pressure, and temperature, until the surfaces coincide. In this way, taking twenty-nine different substances, she completely verifies from experiment van der Waals' law of correspondence. The theory of van der Waals has been one of the greatest importance in directing experimental investigation, and in attacking the difficult problems of the liquefaction of the most permanent gases. One of its greatest triumphs has been the proof that the critical constants and the boiling-point of hydrogen theoretically deduced by Wroblewski from a study of the isothermals of the gas taken far above the temperature of liquefaction are remarkably near the experimental values. We may safely infer, therefore, that if hereafter a gas be discovered in small quantity even four times more volatile than liquid hydrogen, yet by a study of its isothermals at low temperature we shall succeed in finding its most important liquid constants, although the isolation of the real liquid may for the time be impossible. It is perhaps not too much to say that as a prolific source of knowledge in the department dealing with the continuity of state in matter, it would be necessary to go back to Carnot's cycle to find a proposition of greater importance than the theory of van der Waals and his development of the law of corresponding states.

It will be apparent from what has just been said that, thanks to the labours of Andrews, van der Waals, and others, theory had again far outrun experiment. We could calculate the constants and predict some of the simple physical characteristics of liquid oxygen, hydrogen, or nitrogen with a high degree of confidence long before any one of the three had been obtained in the static liquid condition permitting of the experimental verification of the theory. This was the more tantalising, because, with

whatever confidence the chemist may anticipate the substantial corroboration of his theory, he also anticipates with almost equal conviction that as he approaches more and more nearly to the zero of absolute temperature, he will encounter phenomena compelling modification, revision, and refinement of formulæ which fairly covered the facts previously known. Just as nearly seventy years ago chemists were waiting for some means of getting a temperature of 100 degrees below melting ice, so ten years ago they were casting about for the means of going 100 degrees lower still. The difficulty, it need hardly be said, increases in a geometrical rather than in an arithmetical ratio. Its magnitude may be estimated from the fact that to produce liquid air in the atmosphere of an ordinary laboratory is a feat analogous to the production of liquid water starting from steam at a white heat, and working with all the implements and surroundings at the same high temperature. The problem was not so much how to produce intense cold as how to save it when produced from being immediately levelled up by the relatively superheated surroundings. Ordinary non-conducting packings were inadmissible because they are both cumbrous and opaque, while in working near the limits of our resources it is essential that the product should be visible and readily handled. It was while puzzling over this mechanical and manipulative difficulty in 1892 that it occurred to me that the principle of an arrangement used nearly twenty years before in some calorimetric experiments, which was based upon the work of Dulong and Petit on radiation, might be employed with advantage as well to protect cold substances from heat as hot ones from rapid cooling. I therefore tried the effect of keeping liquefied gases in vessels having a double wall, the annular space between being very highly exhausted. Experiments showed that liquid air evaporated at only one-fifth of the rate prevailing when it was placed in a similar unexhausted vessel, owing to the convective transference of heat by the gas particles being enormously reduced by the high vacuum. But, in addition, these vessels lend themselves to an arrangement by which radiant heat can also be cut off. It was found that when the inner walls were coated with a bright deposit of silver the influx of heat was diminished to one-sixth the amount entering without the metallic coating. The total effect of the high vacuum and the silvering is to reduce the ingoing heat to about 3 per cent. The efficiency of such vessels depends upon getting as high a vacuum as possible, and cold is one of the best means of effecting the desired exhaustion. All that is necessary is to fill completely the space that has to be exhausted with an easily condensable vapour, and then to freeze it out in a receptacle attached to the primary vessel that can be sealed off. The advantage of this method is that no air-pump is required, and that theoretically there is no limit to the degree of exhaustion that can be obtained. The action is rapid, provided liquid air is the cooling agent, and vapours like mercury, water, or benzol are employed. It is obvious that when we have to deal with such an exceptionally volatile liquid as hydrogen, the vapour filling may be omitted because air itself is now an easily condensable vapour. In other words, liquid hydrogen, collected in such vessels with the annular space full of air, immediately solidifies the air, and thereby surrounds itself with a high vacuum. In the same way, when it shall be possible to collect a liquid boiling on the absolute scale at about 5 degrees, as compared with the 20 degrees of hydrogen, then you might have the annular space filled with the latter gas to begin with, and yet get directly a very high vacuum, owing to the solidification of the hydrogen. Many combinations of vacuum vessels can be arranged, and the lower the temperature at which we have to operate the more useful they become. Vessels of this kind are now in general use, and in them liquid air has crossed the American continent. Of the various forms, that variety is of special importance which has a spiral tube joining the bottom part of the walls, so that any

liquid gas may be drawn off from the interior of such a vessel. In the working of regenerative coils such a device becomes all-important, and such special vessels cannot be dispensed with for the liquefaction of hydrogen.

In the early experiments of Pictet and Cailletet, cooling was produced by the sudden expansion of the highly compressed gas preferably at a low temperature, the former using a jet that lasted for some time, the latter an instantaneous adiabatic expansion in a strong glass tube. Neither process was practicable as a model of producing liquid gases, but both gave valuable indications of partial change into the liquid state by the production of a temporary mist. Linde, however, saw that the continuous use of a jet of highly compressed gas, combined with regenerative cooling, must lead to liquefaction on account of what is called the Kelvin-Joule effect; and he succeeded in making a machine, based on this principle, capable of producing liquid air for industrial purposes. These experimenters had proved that, owing to molecular attraction, compressed gases passing through a porous plug or small aperture were lowered in temperature by an amount depending on the difference of pressure and inversely as the square of the absolute temperature. This means that for a steady difference of pressure the cooling is greater the lower the temperature. The only gas that did not show cooling under such conditions was hydrogen. Instead of being cooled it became actually hotter. The reason for this apparent anomaly in the Kelvin-Joule effect is that every gas has a thermometric point of inversion above which it is heated and below which it is cooled. This inversion point, according to van der Waals, is six and three-quarter times the critical point. The efficiency of the Linde process depends on working with highly compressed gas well below the inversion temperature, and in this respect this point may be said to take the place of the critical one, when in the ordinary way direct liquefaction is being effected by the use of specific liquid cooling agents. The success of both processes depends upon working within a certain temperature range, only the Linde method gives us a much wider range of temperature within which liquefaction can be effected. This is not the case if, instead of depending on getting cooling by the internal work done by the attraction of the gas molecules, we force the compressed gas to do external work as in the well-known air machines of Kirk and Coleman. Both these inventors have pointed out that there is no limit of temperature, short of liquefaction of the gas in use in the circuit, that such machines are not capable of giving. While it is theoretically clear that such machines ought to be capable of maintaining the lowest temperatures, and that with the least expenditure of power, it is a very different matter to overcome the practical difficulties of working such machines under the conditions. Coleman kept a machine delivering air at *minus* 83 degrees for hours, but he did not carry his experiments any further. Recently Monsieur Claude, of Paris, has, however, succeeded in working a machine of this type so efficiently that he has managed to produce one litre of liquid air per horse power expended per hour in the running of the engine. This output is twice as good as that given by the Linde machine, and there is no reason to doubt that the yield will be still further improved. It is clear, therefore, that in the immediate future the production of liquid air and hydrogen will be effected most economically by the use of machines producing cold by the expenditure of mechanical work.

(To be continued).

Appointment.—The Governors of the Northern Polytechnic Institute have appointed Mr. W. H. Mills, M.A., Ph.D., Fellow of Jesus College, Cambridge, as Head of the Chemical Department, to succeed Mr. H. C. L. Bloxam, who resigned the position in order to take up an appointment in Cape Town.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. BELFAST, 1902.

By EDWARD DIVERS, M.D., D.Sc., F.R.S., V.P.C.S.,
Emeritus Professor of Chemistry in the Imperial University of Tokyo,
Japan.

President of the Section.

THE ATOMIC THEORY WITHOUT HYPOTHESIS.

IN opening the Chemical Section of the British Association in this city and in the halls of the Queen's College, my first words must be those of reverence for the memory of Thomas Andrews, for so many years the Professor of Chemistry in this College, whose investigations into the properties of gases—above all, those which resulted in the recognition and determination of the critical pressure and temperature of carbonic anhydride—have become a part of the foundation of the Kinetic Theory of Gases. At the meeting of the British Association here in 1852 Andrews was President of this Section, and again at the meeting in Edinburgh in 1871.

Since the meeting last year another distinguished chemist, formerly professor in one of the Queen's Colleges, Maxwell Simpson, has also passed away. He, too, acted as President of this Section, namely, at the meeting in Dublin in 1878. The work by which Simpson's name will ever be recalled is more especially that upon the synthesis of polybasic organic acids.

One other name must not be left unmentioned in this Address: it is that of a long-time Fellow of the Chemical Society who has been intimately connected with the British Association—I mean that of George Griffith, the genial and most effective Assistant General Secretary of the Association for so many years, who died four months ago. He had visited Belfast in the spring and made the preliminary arrangements with the Local Committee for this meeting. He joined the Chemical Society in 1859—just one year before I did—and remained a Fellow until his death.

It is now almost a century ago since John Dalton came known to the world his theory of the nature of chemical combination by the publication of a table of atomic weights. He had been occupying himself for some years with the study of the physical properties and atomic constitution of gases before he was led to extend the notion of the atom to chemical phenomena, and thus to form that conception which was to become celebrated as the atomic theory. In his laboratory note-books, preserved from 1802 onwards, the publication and analysis of which we owe to Sir Henry Roscoe and Dr. Harden, no reference is made to the theory till 1803, but we may well believe with Henry that it was already in Dalton's mind just a hundred years ago. But however that may have been, it seems fitting in a year so closely approaching the centennial of its publication as the present that the occupier of this Chair should address his audience on a subject of such general interest and importance as the atomic theory, if indeed there remains anything to be said on a subject which has so long and so fully engaged attention.

I dare not assert that I have found anything actually novel to bring before you with regard to the atomic theory, but I may say that there has certainly long seemed to me to exist the need to treat it as being a true theory instead of as an hypothesis, and to teach it and discuss it accordingly.

In thus setting forth what appears to me to be the proper form of the atomic theory, I shall have, at the risk of overtaxing your patience, to re-state and examine most of the fundamental and familiar principles of our science in order to illustrate and justify the view I take. Not only this, but in order as directly and briefly as possible to meet the objection that, whatever the atomic theory may be, it cannot be introduced to the student of chemical philosophy in another form than that now in use, I

shall sometimes have to adopt, in order to show what can be done, a didactic method which, in most other circumstances, would be quite inexcusable before so distinguished an assembly.

The atomic theory of chemistry stands unsurpassed for the way in which it has fulfilled the purpose of every great theory, that of giving intellectual mastery of the phenomena of which it treats. But in the form in which it was enunciated, and still is universally expressed and accepted, it has the defect of resting upon a metaphysical basis, namely, upon the ancient hypothesis that bodies are not continuous in texture, but consist of discrete, ultra-minute particles whose properties, if known, would account for those of the bodies themselves. Hence it has happened that, despite the light it throws upon the relations of chemical phenomena and the simple means it affords of expressing these relations, this theory has always been regarded with misgiving, and failed to achieve that explicit recognition which its abounding merit calls for. Indeed, the desire has been expressed to see the time when something on a more solid foundation shall have taken its place.

Now, it is not my intention to discuss the merits or demerits of the atomic hypothesis, which can indeed no longer be treated as a merely metaphysical speculation. What I would do to-day is to impress upon you that, in spite of all that has been said and written about the atomic hypothesis in connection with chemistry, the atomic theory propounded by Dalton and adopted, implicitly at least, by all chemists, is not founded upon the metaphysical conception of material discontinuity, and is not explained or illuminated by it. For if that should be the case there will no longer exist any grounds for hesitation in accepting the theory quite explicitly, and then the anomalous condition of things will be removed of a theory being in universal use without its truth being freely and openly admitted. For the sake of clearness, it is convenient to restrict the term "atomic hypothesis" to the old metaphysical view of the discontinuity of matter whilst applying the term "atomic theory" to the current elaborated form of the Daltonian theory; this distinction is adhered to in the present Address.

In the peroration to his admirable discourse upon atomic weights or masses delivered before the Chemical Society in 1892 as the Stas Memorial Lecture, Professor Mallet, F.R.S., said:—"By the chemist at his balance the arm of reason is directed into those regions of almost inconceivable minuteness, which lie as far beyond the reach of the most powerful microscope as that carries us beyond the reach of the naked eye, quite as impressively as that same arm is stretched forth by the astronomer at his divided circle to reach and to weigh the mighty planets that shine in the remotest regions of our solar system." On two occasions I have heard the same comparison between the chemist and the astronomer made by Lord Kelvin when he was in the company of chemists; and undoubtedly both these high authorities have only then expressed the general view as to the nature of the domain of the chemist. Yet I venture to question whether there is anything in the ways and works of the chemist to support such a view and give point to Mallet and Kelvin's comparison. If, indeed, chemistry is a science which rests upon the atomic hypothesis and, therefore, would cease to exist in the form into which it has developed, should matter prove to be continuous and not discrete, nothing can be said against the view that it is a science of the minute. But I am sure there can be no one ready to maintain that, if the hypothesis of the atomic constitution of substances were an unfounded one, the atomic theory would have been a discovery of no great importance; and Dalton himself, instead of being the founder of the chemistry of to-day, have been little more than the discoverer of the law of multiple proportions. If that cannot be maintained, what, then, becomes of this conception of chemistry as dealing with the minute? So far as comparison can be made between the operations of

the astronomer and the chemist, it is the former and not the latter who, as a matter of fact, deals with the almost infinitely minute. For if, indeed, the chemist often works upon comparatively small amounts of substances, and, consequently, with very sensitive balances, that is, as we all know, only for reasons of economy of time, materials, and apparatus; otherwise he works on the largest possible scale, with the object of attaining to the highest degree of accuracy and perfection. The astronomer, on the other hand, has, perforce, to deal with the smallest visible things in nature, the nearest approach there is to geometrical points, those fixed points of light in the heavens which are only known through scientific investigation to be other than what they seem to be. It is, therefore, only as interpreted by the atomic hypothesis that chemistry can be said to deal with the minute.

When the atomic theory is expounded in the usual way it is commonly and correctly stated that, on the assumption that substances consist of minute indivisible particles having weights or masses bearing the ratios of the combining numbers assigned to them, the laws of chemical combination by weight necessarily follow, and are thereby explained. But then the converse is not true—that, because chemical combination obeys the well-known laws, substances consist of discrete particles. Nor does the assumption of the truth of the atomic hypothesis afford any real explanation of the facts expressed by the laws of chemical combination, or more comprehensively by the atomic theory, when that theory is given in non-hypothetical terms. It is just as difficult to see why the atoms should possess the weights on chemical grounds assigned to them, as to see why substances interact in the proportions that they do; that they do so is, in either case, an ultimate fact, for which no explanation has presented itself. The atomic hypothesis masks this ignorance and deadens inquisitiveness. Notwithstanding all this, which is incontrovertible, it is certainly a common opinion that in chemistry we investigate the minute and intimate constitution of things.

But if, after all, chemistry does not deal with the minute, or, rather, if it has no concern with the magnitude of single bodies or their molecules; if the atomic hypothesis is not the foundation of, or necessary to, the atomic theory, then it is certainly most desirable and important that the theory of chemistry, which, with all its modern developments, I take to be indisputably the atomic theory of Dalton, should be held and expounded without any reference to the physical constitution of matter, in so far as that remains unknown. The opinion that chemical theory should be developed without reference to the atomic hypothesis has indeed all along been held by many eminent chemists; but then the dilemma appears to have presented itself to them, that either the atomic hypothesis must be granted, or the atomic theory must be dispensed with, since it falls with the hypothesis. That dilemma I do not recognise, and the practice of chemists shows beyond doubt that it is always ignored. Investigators use the theory, whether they admit it or not; teachers of the science find it indispensable to their task, however much they may deprecate, and rightly so, unreserved acceptance of the atomic hypothesis as true.

Refusing to commit themselves to belief in the hypothesis, chemists have thought from the first to escape the adoption of the atomic theory by putting Dalton's discovery into something like these words:—Numbers, called proportional or combining numbers, can be assigned to the chemical elements—one to each—which will express all the ratios of the weights or masses in which substances interact and combine together. Perhaps the atomic theory is here successfully set aside by expressing what is an actuality as an unaccounted for possibility. But then those who use any such mode of expressing the facts, without reference to the theory, never fail also to adopt the doctrine of equivalents, and thus, by this double act, implicitly give in their adherence to the theory.

Divested of all reference to the physical constitution of

matter, the atomic theory is that the quantities of substances which interact in single chemical changes are equal to one another,—as truly equal in one way as equal masses are in another,—and, therefore, that chemical interaction is a measure of quantity of unlike substances, distinct from, and independent of, dynamical or mass measurement.

Dalton, indeed, did not express himself in any such terms, his mind being fully possessed with the ancient and current belief upon which he framed his theory that substances are made up of minute, discrete particles. But it is clear enough that his theory was that of the existence of another order of equality between substances than that of weight. Up to this time, the weight or mass of every ultimate particle of any substance whatever appears to have been assumed to be the same, the atoms being alike in every way. That assumption is still made by many thinkers, chemists among them; we meet it, for example, in the different forms of the hypothesis that the elements are all, in some way, physically compounded of a universal and only true element, as in Prout's hypothesis. Dalton saw things differently, and recognised that, on the assumption of substances being constituted of particles which never subdivide, weight or mass cannot be the same for every such particle, except in the case of those of any one simple substance. Therefore, having given some numbers showing what he believed to be the respective weights of the atoms of several simple substances, taking that of hydrogen as of unit-weight, he proceeded at once to invent symbols for these atoms to indicate, not only their distinctness in kind, but above all things their indivisibility and their equality, properties which the use of their atomic numbers would have inadvertently concealed or even apparently denied, and could never have expressed or connoted.

It was only in this immediate invention and use of chemical symbols that Dalton's conception found clear expression; and again it is by the universal adoption of such symbols that chemists have shown their real acceptance of the atomic theory, even while displaying, not infrequently, their scepticism as to its truth. The replacement by Berzelius of Dalton's marked circles for atomic symbols by letters which should recall the names of the substances was in a way a great improvement, but it has had the serious consequence of causing chemical symbols to be usually first brought under notice merely as serviceable abbreviations for the names of the elements, and only then described as representing their atomic quantities. Now, evidently, what the character used as symbol shall be is, theoretically considered, but a petty detail; the vital point is what the character symbolises, and that is the atom. It does not symbolise the name; it only indicates that and recalls it. It may be said indeed to represent the atomic number, since it stands in place of it; but it is made to do so only in order that we may for the time forget this number and have in mind the integral character of the atom. It is not the 4006 parts of sodium hydroxide and 8097 parts of hydrobromic acid, or approximately twice as much of the latter as of the former; it is not these gravimetrically expressed interacting quantities that we are to think of when the formulæ NaOH and HBr are before us, as we too often strive to do; it is not these from a chemical point of view, meaningless numbers of parts, but quantities which are equal in the sense of chemistry, that are expressed as such by these symbolic formulæ. The real purpose of chemical formulation is not to abbreviate or replace language, but to facilitate, if not ensure, abstraction from and non-contemplation of gravimetric numbers.

I have just passed from atomic symbols to the formulæ of molecules; but this was not without warrant. In the form in which I have enunciated the atomic theory, it relates to the chemical interaction of substances, whether compound or simple, and the equality of the quantities concerned is the equality of molecules, since these are the quantities of substances entering into or coming out

from single chemical interactions. Were it not, therefore, for fear of confounding it with the mechanical theory of that name, the atomic theory should be called the molecular theory of chemistry. It might, indeed, have happened to be so called by its author, for Dalton has told us that he had in mind both atom and molecule as names for his chemically ultimate particles, and chose the former because it carried with it the notion of indivisibility. He extended also, as we do, the use of the term "atom" to chemically compound substances, since their combining quantities are chemically indivisible.

Next, I would point out that in the atomic theory the notions of indivisibility and equality are inseparably involved. The indivisibility of atom and molecule is not absolute or ultimate, and Dalton distinctly guarded himself against being understood to claim for the atom more than chemical indivisibility, and chemists of to-day assert no more than this. This indivisibility being conditioned by the equality of molecules, the importance of emphasising it rests only upon the danger, when it is overlooked, of losing sight also of the chemical equality through the gravimetric inequality receiving numerical expression, and thereby conveying the notion of divisibility, though only gravimetrically. The idea of indivisibility in connection with the atom or molecule is intrinsically quite subordinate to that of equality; for equality, being unity or oneness brought into relation with itself, the conception of it carries with it and includes that of indivisibility. Any rational hypothesis as to substances consisting of ultimate particles will include the notion of their being indivisible particles; and the import of the hypothesis in chemical theory must lie, therefore, not in this indivisibility, but in the nature of the equality of the particles. By his atomic theory Dalton asserted that where the substances are different this equality is chemical instead of gravimetric.

Molecules are equal in the sense that they are quantities of their substances which are interdependent and co-ordinate in any and every single chemical change in which they take part together. It is a form of equality for which no close parallel can be found; but as to that it should be remembered that this equality relates to the phenomena of the transformations of substances into each other, which, though they form so large a part of the phenomena of the universe, are fundamentally distinct in nature from the rest of the behaviour of bodies throughout which the substance remains what it was. In some agreement with it there is that of mechanical pressures when these balance or neutralise each other, and therefore are opposite and mutually destructive though equal. But such pressures when exerted in the same direction are also equal in their effect on any body in their path, whereas in chemical interactions the effects of molecules or equal quantities of two unlike substances are only equal in the sense that each is that quantity which interacts with the same quantity of some third substance, which itself proves to be also a chemically equal quantity to them. For the products of the interaction in the one case are in part at least not the same as those in the other, though all prove chemically equal in further interactions.

To give an example, the molecule of ammonia is equal to that of aldehyde in that it combines with it and with it disappears, or ceases to exist as such. For the same reason it is equal to the molecule of hydrocyanic acid, and molecules of aldehyde and hydrocyanic acid equal to each other, because they, too, combine and disappear as such in doing so. But the molecule of ammonia again equals that of aldehyde in effecting transformation of hydrocyanic acid and its own self into something else. And lastly, chemically equal or molecular are the products of these combinations; aldehyde ammonia, ammonium cyanide, and aldehyde-cyanhydrine, not only among themselves, but also with the quantities of ammonia, aldehyde, and hydrocyanic acid from which they come and into which they return in other chemical changes. But with all this quantitative equality in trans-

forming power, the substances produced are unlike and, each to each, peculiar to one of the three acts of chemical combination; and on this account exception may be taken to the treatment of molecules as equal chemical quantities. Yet the equality of molecules here asserted is but an extension of what is meant by the equivalence of certain atoms and radicals, since the atom and the radical are, nowadays, conceptions entirely dependent upon and derived from that of the molecule (apart, of course, from the atomic hypothesis); and this universally allowed equivalence admittedly does not extend to the identity of the products of the replacing activity of the atoms and radicals.

Quantitative equality and equivalency, it is true, have not the same meaning, equivalence being used to denote qualified equality, equality in certain specified ways, of quantities not equal in all other ways and possibly in no other. Quantities of different substances cannot, strictly speaking, ever be equal, and can only be styled so in the sense of being equivalent; for were they equal in every way the substances would obviously be the same. But this fact, if it ever strikes one, is ignored by universal custom, and quantities of substances, however unlike—feathers, air, water, salt, and what not—are taken to be all equal, even by chemists as by the world at large, if only they have the same weight, notwithstanding the incongruities of the substances. I proceed now to show the baselessness of this conviction, but only to bring out more strongly the claim of chemical activity to equal rights with weight or mass in determining what are equal quantities of substances, for I am aware that here I have nothing to tell you that you do not already know. Weight being only the gravitational measure of mass, which itself is independent of it, quantities of substances are held to be equal, when their masses are equal. Now, mass is quantity of matter. But what then is meant by matter? The answer must be either that it is a general term for any and all substances, or 'else that it is the common basis of all substances, which presents itself in all the different forms which are known to us as such, by virtue of a corresponding variety in its intestinal motions. I gladly pass over the latter answer without discussing it, on the ground that it introduces the subject of the intimate constitution of substances, which it is my set purpose to keep independent of in this discourse. I will only say of it that it would probably be the answer of many physicists and chemists, and yet that it gives such a limitation to the nature of matter as makes the common expression "constitution of matter" devoid of all meaning. That expression means, and can only mean, the constitution of substances in common; and this brings me to the first answer, that matter is the term standing for all substances in common. Now, one thing which all substances possess in common is the property of resisting pressures; pressures not only of moving bodies, but of the motions of the ether and electrons. Measured or quantified, resistance becomes mass, all that can be signified by this term being the quantity of the resistance or inertia a substance exhibits when tested. It is the measure of a property of the substance, that is all; and there is no other way of quantifying a substance than through some one of its properties. No quantities of different substances can, as such, be commensurable throughout; and when compared and measured through some common property, such as the possession of mass, the equivalence or pseudo-equality found by this means is not the same as that found when some other common property is taken as the means of measurement. But experience has shown that though there are several rational and comprehensive ways of instituting, through some common property, comparisons between quantities of different substances, they all, with the exception of that of weighing, agree more or less exactly in pointing to the same order of equivalence, that of chemical activity; for with this are colligated those of gaseous volume and the other well-known physical activities, which give nearly the same quantities

as it gives of different substances as being molecularly equivalent. There are, therefore, essentially only two measures of quantitative equivalency or pseudo-equality between substances, the dynamical and the chemical or molecular, the one wholly independent of and the other wholly dependent upon the particular nature of the substances compared. The former is the measure of dynamical phenomena, those of changes of bodies, due to their impacts and pressures, which may lead to their deformation and disruption, but do not involve transformations of the substances of the bodies into others; the latter is the measure of chemical phenomena, those of changes of bodies induced by such of their interactions as do involve transformations of the substances of the interacting bodies into other substances. Since it is already settled for us by custom that quantities of different substances are to be called equal when or because they are equivalent gravimetrically, and as it is not to be supposed that we shall ever give up calling 16 kilos. of oxygen, of salt, of chalk, and of every other substance, however unlike, equal quantities of them from the gravimetric point of view, we have no choice but also to call molecular quantities of these substances equal from the chemical point of view, if the claim to co-ordination in equality of chemical with gravimetric equivalency is to be asserted and maintained.

(To be continued).

ATOMIC WEIGHT STANDARDS AND PROUT'S HYPOTHESIS.

(PRELIMINARY NOTICE).

By CECIL HOLLINS.

THE reason for the failure of all attempts to express the atomic weights as integers probably lies in the fact that the units chosen so far have not been suitable ones.

Hydrogen was first adopted as the standard because it was the lightest element known. Owing to the difficulty of making direct determinations with this element, an oxygen standard seemed more desirable; accordingly the atomic weight of O was raised from 15.88 to 16.00, thus lowering the unit to 0.9925 of the atomic weight of H. In this scale the atomic weights of the elements exhibit a considerable tendency to agree with Prout's whole-number hypothesis. This is shown in Table I.

TABLE I.

(For sixty-seven elements).

	H=1.	O=16.
Number of integral atomic weights..	6	18
Sum of deviations from integers ..	15.861	10.298

So, by further lowering the unit, we might expect that the atomic weights of the elements would still more nearly approach to integers. Of course, it was useless to attempt to find the G.C.M., but by dividing each atomic weight into the nearest whole number, factors were obtained varying between 1.0101 for He and 0.9859 for Si, the mean being 0.99877. If this be taken as the unit, the atomic weights of the elements show a further tendency to become integral; and, by treating these in the same way, the total deviation is again reduced (the mean factor now = 0.99867). The results for seventeen elements upon whose atomic weights most authorities agree, are given in Table II.

I am engaged in further investigation of the subject, but even as the table stands there is some encouragement shown; for the probability that the total deviation in the last column should not be greater than 0.729 is only 1 in 4×10^{12} ; and even when the elements of atomic weight less than 27 are eliminated, the chances are still 1000 to 1 against the total deviation not being greater than it is.

Possibly the approximate G.C.M. of the factors will give better results than their mean, but this I leave for a

TABLE II.
Atomic weights.

	H=1.	O=16.	Factor 0.99877.	Factor 0.99867.
H	1.00	1.008	1.007	1.005
He	3.93	3.96	3.955	3.950
Li	6.97	7.03	7.021	7.011
Na	22.88	23.05	23.022	22.991
K	38.82	39.11	39.062	39.010
O	15.88	16.00	15.980	15.960
S	31.83	32.07	32.030	31.997
Se	78.6	79.2	79.102	78.997
N	13.93	14.04	14.023	14.004
F	18.91	19.05	19.026	19.002
Cl	35.18	35.45	35.406	35.359
C	11.9	12.0	11.985	11.969
Cr	51.7	52.1	52.036	51.967
Be	9.0	9.1	9.059	9.077
Ca	39.8	40.1	40.080	40.027
Al	26.9	27.1	27.066	27.030
B	10.9	11.0	10.986	10.971
Number of integral atomic weights*..	3	6	10	15
Total deviation from integers	2.87	1.448	1.064	0.729

* Correct to one decimal place.

further paper, in which I hope to bring the atomic weights of *all* the elements as near to integers as the seventeen enumerated above.

NOTE ON CEMENT ANALYSIS.

By R. F. YOUNG and B. F. BAKER.

It is often desirable in cement analysis to estimate only CaO. The usual method of procedure is to dissolve the cement in dilute HCl, add excess of AmOH to precipitate silica, Al_2O_3 , and Fe_2O_3 , precipitate the calcium as oxalate, and ignite to CaO.

This method has been found by the authors to give an entirely erroneous result, which may be as much as 1.5 per cent too high or too low.

The reason of this, in our opinion, is that when cement is dissolved in dilute HCl, part of the calcium silicate is not decomposed, but merely dissolves and is precipitated on neutralising the acid with ammonia. This causes a low result; but, on the other hand, the ignited CaO will invariably contain very appreciable quantities of SiO_2 , Al_2O_3 , and Fe_2O_3 , which will cause a high result.

The two following methods have been found to give very satisfactory results:—

I. One grm. of the cement is treated in a conical beaker with a small quantity of concentrated HCl. A little HNO_3 is added, and the contents evaporated to dryness on a sand-bath, and heated till the contents are distinctly red; then treated with dilute HCl, and excess of ammonia added. The SiO_2 , $\text{Al}_2(\text{OH})_6$, and $\text{Fe}_2(\text{OH})_6$ are filtered off, and the calcium precipitated as oxalate and ignited to CaO in the usual way.

II. One grm. of cement is dissolved in dilute HCl, AmOH added, and the precipitate of iron, alumina, and silica filtered off. This precipitate is re-dissolved in concentrated HCl and re-precipitated by AmOH. The two filtrates and washings are collected, and the calcium estimated as above.

In accurate estimations, it is advisable in both methods to dissolve the ignited CaO after weighing in HCl, and estimate the SiO_2 , Al_2O_3 , and Fe_2O_3 it may contain.

We may mention that we have tried the volumetric estimation of calcium by titrating the excess of a known quantity of standard oxalic acid left after precipitating in ammoniacal solution, and have found it invariably gives

low results. This seems to point to the fact that all the calcium is not precipitated as oxalate.

The Laboratory,
Wouldham Cement Co. (1900),
West Thurrock, Essex.

ON THE PRESENCE OF LIME AS DOLOMITE
IN CERTAIN CULTIVATED SOILS.

By Dr. T. L. HIPSON.

In a recent examination of certain cane soils from Argentina, yielding only from 8 to 20 tons of cane to the acre, I have met with a singular result, which may partly account for this deficiency, and does not appear to have ever been noticed before.

These soils, of which I have made the complete analysis of eight specimens taken with great care at a depth of 1 foot from the surface, have as their basis a micaceous sand, with little clay, a good amount of nitrogenous humus, and all the physical and chemical elements of fertility; but the lime, which amounts to no less than 1 per cent, appears not to have been affected after ten or twelve years' constant cultivation and cropping. Here are the figures for lime and magnesia:—

	Lime.	Magnesia.
1. Cultivated ten years. Yield 15 tons.	1.12	1.08
2. Same soil, uncultivated	1.12	1.09
3. Another plantation, same district. Cultivated twelve years. Yield, 20 tons	1.10	1.08
4. The same from an uncultivated region	1.11	1.09
5. Another plantation, cultivated several years. Yield, 8 tons.	1.12	1.02
6. Same land, uncultivated	0.95	0.80

It is evident from these results that the lime is present as *dolomite*, which is not readily assimilated.

The phosphoric acid in these soils amounts to about 0.08 per cent, and the alkalis to about 0.12; whilst the humus averages 4 per cent, and the insoluble rock (sand, with golden mica passing into white mica, and a little clay) 70 to 84 per cent.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

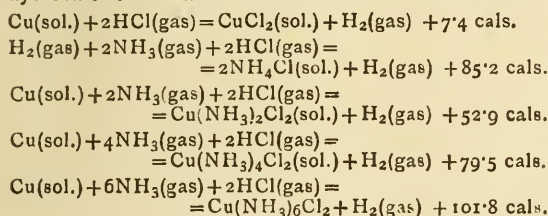
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 5, August 4, 1902.

Direct Hydrogenation of the Oxides of Nitrogen by the Method of Contact.—Paul Sabatier and J. B. Senderens.—It has been known for some time that finely divided platinum will provoke direct reduction of several nitrogen oxides by means of hydrogen. The authors now perform a series of experiments on the action of reduced nickel and copper in order to investigate a general method of hydrogenation for the volatile organic compounds, and particularly nitrogen derivatives. They find the action of reduced nickel and copper the same as that of spongy platinum.

Gentibiose. Preparation and Properties of Crystalline Gentibiose.—Em. Bourquelot and H. Hérissé. —Previous researches established the fact that gentianose is a hexotriose, $\text{C}_{18}\text{H}_{32}\text{O}_{16}$, which, when treated with invertine or very dilute boiling sulphuric acid, is decomposed, giving one molecule of levulose and one molecule of a hexobiose, which the authors called gentibiose. This latter substance they now investigate more fully. They find the formula, instead of being $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, to be $\text{C}_{12}\text{H}_{22}\text{O}_{11} + 2(\text{CH}_4\text{O})$; that is to say, the crystals contain 2 mols. of methyl alcohol. The substance can, however, be obtained in an anhydrous state free from alcohol.

Anhydrous Ammoniacal Cupric Chlorides. Cupro-ammonic Radicles.—M. Bouzat.—Different cupric salts, such as chlorides, sulphates, acetates, &c., evolve equal quantities of heat on combining with ammonia. This relation points to the existence of complex radicles forming cupro-ammonic salts. The author now further examines the action of ammonia gas on anhydrous copper salts (chlorides and sulphates). He finds the heat of fixation of the two first molecules of ammonia on to the copper chloride is 45.5 cal., of the next two is 26.6 cal., and of the last two 22.3 cal. The following equations show for each cupro-ammonia radicle the heat of formation and the heat of substitution of the hydrogen in the hydrochloric acid radicle:—



Action of Nitrous Acid in Alkaline Solution on the α -Substituted β -Ketonic Ethers.—M. Bouveault and René Locquin.—The mechanism of the action of nitrous acid on the α -substituted β -ketonic ethers can be stated as follows:—If the reaction takes place under such conditions that the ether group is not saponified, or if is saponified in acid solution, it forms an acid and a substituted oxime of glyoxylic ether. If, during the reaction, the ether group is saponified in such a manner as to give the salt $\text{R}-\text{CO}-\text{CH} < \text{CO}_2\text{M}$, a monoxime of α -diketone and carbonic acid are obtained.

No. 6, August 11.

This number contains no chemical matter.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemistry) at the Belfast Meeting of the British Association:—

President—Prof. Edward Divers, M.D., F.R.S., V.P.C.S.
Vice-Presidents—Prof. P. F. Frankland, F.R.S.; Prof. E. A. Letts, D.Sc., Ph.D.; Prof. W. A. Shenstone, F.R.S.
Secretaries—R. F. Blake; M. O. Forster, D.Sc., Ph.D.; Prof. G. G. Henderson, M.A., D.Sc.; Prof. W. J. Pope, F.R.S. (Recorder).

Committee—W. E. Adeney, D.Sc.; E. F. Armstrong, Ph.D.; G. T. Bellby; C. H. Bothamley; Prof. A. Crum Brown, F.R.S.; Sir C. Cameron, M.D.; D. L. Chapman; Prof. A. E. Dixon, M.D.; F. G. Donnan, D.Sc.; T. Fairley; Prof. J. H. Gladstone, F.R.S.; G. Gladstone; R. T. Glazebrook, D.Sc., F.R.S.; Prof. W. D. Halliburton, F.R.S.; Prof. W. N. Hartley, F.R.S.; P. J. Hartog, B.Sc.; W. J. Heath; A. Hutchinson, M.A., Ph.D.; Francis Jones; Prof. E. Knoevenagel; R. N. Lennox; H. Marshall, D.Sc.; W. S. Mills, M.A.; G. T. Morgan, D.Sc.; H. Ramage, B.A.; Lord Rayleigh, F.R.S.; Sir W. C. Roberts-Austen, K.C.B., F.R.S.; Prof. Senior; J. Smyth; Prof. J. J. Sudborough, D.Sc., Ph.D.; W. Thomson; M. W. Travers, D.Sc.; Prof. D. Vorländer; Prof. J. Wertheimer.

The Papers brought before the Section were as follows:—

President's Address—The Atomic Theory without Hypothesis.

Prof. E. A. Letts and W. Caldwell—On Experiments to ascertain the amount of Carbonic Anhydride absorbed from Sea-water by Air.

Prof. E. A. Letts—On the Corrosion of Copper by Sea-water, and on the Detection of Traces of Impurity in the Commercial Metal.

Prof. F. Clowes, D.Sc.—Action of Distilled Water on Lead.

Dr. A. W. Crossley—Hydro-aromatic Compounds with Single Nucleus.

B. Blount—The Undesirability of establishing Standard Analytical Methods.

Dr. C. E. Fawcitt—The Decomposition of Urea.

Prof. W. N. Hartley—Report of Committee on Absorption Spectra.

Dr. E. F. Armstrong—Recent Synthetical Researches in the Glucoside Group.

Dr. E. F. Armstrong—The Synthetical Action of Enzymes.

W. Ackroyd—The Telluric Distribution of the Elements in relation to their Atomic Weights.

Dr. G. T. Morgan—Our present Knowledge of Aromatic Diazo-compounds.

Miss Ida Smedley—The Colour of Iodine-containing Compounds.

J. Hawthorne—Note on a Fourth Methylmorphimethine.

Prof. T. Purdie and Dr. Irvine—The Alkylation of the Sugars.

Prof. G. G. Henderson—Report of the Committee on preparing Statistics concerning the Training of Chemists employed in English Chemical Industries.

Report of the Committee on Isomeric Naphthalene Derivatives.

Report of the Committee on Isomorphous Sulphonic Derivatives of Benzene.

Major W. E. Edwards, Capt. C. H. Liveing, and Prof. W. R. Hodgkinson—The Reduction of some Metallic Chlorides by Calcium Carbide.

Dr. J. H. Gladstone and W. Hibbert—On Zirconium Hydrate and other Colloids from Elements of the Fourth Group.

Dr. J. H. Gladstone—On Fluorescent and Phosphorescent Diamonds.

Prof. J. J. Sudborough and W. A. Bone—Acid Esters of Methylsuccinic Acids.

II. Hibbert and Prof. J. J. Sudborough—Compounds of Trinitrobenzenes and Alkylated Naphthylamines.

Prof. J. J. Sudborough and K. J. Thompson—Action of Alkalis on Cinnamic Acid Dibromide and its Esters.

Prof. E. A. Letts and J. S. Totton—On the Absorption of Ammonia from Water by Algae.

Prof. E. A. Letts—On Determinations of Atmospheric Carbonic Anhydride made on board the *Discovery* on the Voyage to the Cape and thence to New Zealand.

Prof. R. Meldola—A New Method of causing Isomerisation.

Report of the Committee on the Effect of Gases on Metals.

Report of the Committee on the Nature of Alloys.

Report of the Committee on Preparing a New Series of Wave-length Tables of the Spectra of the Elements.

The Chemical Laboratory Fresenius at Wiesbaden.—During the Summer Term, 1902, the Chemical Laboratory Fresenius was attended by forty-nine Students. Of these, twenty-nine were from Germany, four from England, three from Russia, three from Luxemburg, two from Holland, one from Austria, one from France, one from Belgium, one from Italy, one from Spain, one from Denmark, one from Norway, and one from the Transvaal. There were three Assistants in the Instruction Laboratory, and twenty-four in the Versuchsstationen (private laboratories). To the body of teachers belong the Directors, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Dr. Med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and J. Huber (Architect). The next Winter Term begins on October 15. During the Summer Term, 1902, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen), on behalf of trade, manufacture, mining, agriculture, and hygiene.

NOTES AND QUERIES.

Uses of Litmus-paper.—It seems to me to be very apathetic on the part of litmus-paper manufacturers that they do not advertise it largely as an absolutely necessary adjunct of every householder for use in ascertaining the degree of fermentation in milk when supplied to them in such an injurious and avoidable condition; also amongst dairymen for protection against avoidable souring, semi-fermented milk being supplied and delivered to them by dairy farmers. Such an advertisement ought to appear largely in the daily newspapers. I am widely advising the needed use of litmus-paper for the purpose amongst householders and dairymen.—A. ROBINSON.

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Experimental Chemistry (Inorganic) Prof. H. FRESENIUS, Ph.D.
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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2235.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BELFAST, 1902.

INAUGURAL ADDRESS OF THE PRESIDENT,
PROF. JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S.

(Concluded from p. 144).

Liquid Hydrogen and Helium.

To the physicist the copious production of liquid air by the methods described was of peculiar interest and value as affording the means of attacking the far more difficult problem of the liquefaction of hydrogen, and even as encouraging the hope that liquid hydrogen might in time be employed for the liquefaction of yet more volatile elements, apart from the importance which its liquefaction must hold in the process of the steady advance towards the absolute zero. Hydrogen is an element of especial interest, because the study of its properties and chemical relations led great chemists like Faraday, Dumas, Daniell, Graham, and Andrews to entertain the view that if it could ever be brought into the state of liquid or solid it would reveal metallic characters. Looking to the special chemical relations of the combined hydrogen in water, alkaline oxides, acids, and salts, together with the behaviour of these substances on electrolysis, we are forced to conclude that hydrogen behaves as the analogue of a metal. After the beautiful discovery of Graham, that palladium can absorb some hundreds of times its own volume of hydrogen, and still retain its lustre and general metallic character, the impression that hydrogen was probably a member of the metallic group became very general. The only chemist who adopted another view was my distinguished predecessor, Professor Odling. In his "Manual of Chemistry," published in 1861, he pointed out that hydrogen has chlorous as well as basic relations, and that they are as decided, important, and frequent as its other relations. From such considerations he arrived at the conclusion that hydrogen is essentially a neutral or intermediate body, and therefore we should not expect to find liquid or solid hydrogen possess the appearance of a metal. This extraordinary prevision, so characteristic of Odling, was proved to be correct some thirty-seven years after it was made. Another curious anticipation was made by Dumas in a letter addressed to Pictet, in which he says that the metal most analogous to hydrogen is magnesium, and that probably both elements have the same atomic volume, so that the density of hydrogen, for this reason, would be about the value elicited by subsequent experiments. Later on, in 1872, when Newlands began to arrange the elements in periodic groups, he regarded hydrogen as the lowest member of the chlorine family; but Mendeleeff in his later classification placed hydrogen in the group of the alkaline metals; on the other hand, Dr. Johnstone Stoney classes hydrogen with the alkaline earth metals and magnesium. From this speculative divergency it is clear no definite conclusion could be reached regarding the physical properties of liquid or solid hydrogen, and the only way to arrive at the truth was to prosecute low-temperature research until success attended the efforts to produce its liquefaction. This result I definitely obtained in 1898. The case of liquid hydrogen is, in fact, an excellent illustration of the truth already referred to, that no theoretical forecast, however apparently justified by analogy, can be finally accepted as true until confirmed

by actual experiment. Liquid hydrogen is a colourless transparent body of extraordinary intrinsic interest. It has a clearly defined surface, is easily seen, drops well, in spite of the fact that its surface tension is only the thirty-fifth part of that of water, or about one-fifth that of liquid air, and can be poured easily from vessel to vessel. The liquid does not conduct electricity, and, if anything, is slightly diamagnetic. Compared with an equal volume of liquid air, it requires only one-fifth the quantity of heat for vaporisation: on the other hand, its specific heat is ten times that of liquid air or five times that of water. The coefficient of expansion of the fluid is remarkable, being about ten times that of gas; it is by far the lightest liquid known to exist, its density being only one-fourteenth that of water; the lightest liquid previously known was liquid marsh-gas, which is six times heavier. The only solid which has so small density as to float upon its surface is a piece of pith wood. It is by far the coldest liquid known. At ordinary atmospheric pressure it boils at *minus* 252.5 degrees or 20.5 degrees absolute. The critical point of the liquid is about 29 degrees absolute, and the critical pressure not more than fifteen atmospheres. The vapour of the hydrogen arising from the liquid has nearly the density of air—that is, it is fourteen times that of the gas at the ordinary temperature. Reduction of the pressure by an air-pump brings down the temperature to *minus* 258 degrees, when the liquid becomes a solid resembling frozen foam, and this by further exhaustion is cooled to *minus* 260 degrees, or 13 degrees absolute, which is the lowest steady temperature that has been reached. The solid may also be got in the form of a clear transparent ice, melting at about 15 degrees absolute, under a pressure of 55 m.m., possessing the unique density of one-eleventh that of water. Such cold involves the solidification of every gaseous substance but one that is at present definitely known to the chemist, and so liquid hydrogen introduces the investigator to a world of solid bodies. The contrast between this refrigerating substance and liquid air is most remarkable. On the removal of the loose plug of cotton-wool used to cover the mouth of the vacuum vessel in which it is stored, the action is followed by a miniature snowstorm of solid air, formed by the freezing of the atmosphere at the point where it comes into contact with the cold vapour rising from the liquid. This solid air falls into the vessel and accumulates as a white snow at the bottom of the liquid hydrogen. When the outside of an ordinary test-tube is cooled by immersion in the liquid, it is soon observed to fill up with solid air, and if the tube be now lifted out a double effect is visible, for liquid air is produced both in the inside and on the outside of the tube—in the one case by the melting of the solid, and in the other by condensation from the atmosphere. A tuft of cotton-wool soaked in the liquid and then held near the pole of a strong magnet is attracted, and it might be inferred therefrom that liquid hydrogen is a magnetic body. This, however, is not the case: the attraction is due neither to the cotton-wool nor to the hydrogen—which indeed evaporates almost as soon as the tuft is taken out of the liquid—but to the oxygen of the air, which is well known to be a magnetic body, frozen in the wool by the extreme cold.

The strong condensing powers of liquid hydrogen afford a simple means of producing vacua of very high tenuity. When one end of a sealed tube containing ordinary air is placed for a short time in the liquid, the contained air accumulates as a solid at the bottom, while the higher part is almost entirely deprived of particles of gas. So perfect is the vacuum thus formed, that the electric discharge can be made to pass only with the greatest difficulty. Another important application of liquid air, liquid hydrogen, &c., is as analytic agents. Thus, if a gaseous mixture be cooled by means of liquid oxygen, only those constituents will be left in the gaseous state which are less condensable than oxygen. Similarly, if this gaseous residue be in its turn cooled in liquid hydrogen a still further separation will be effected, everything that is less

volatile than hydrogen being condensed to a liquid or solid. By proceeding in this fashion it has been found possible to isolate helium from a mixture in which it is present to the extent of only one part in one thousand. By the evaporation of solid hydrogen under the air-pump we can reach within 13 or 14 degrees of the zero, but there or thereabouts our progress is barred. This gap of 13 degrees might seem at first sight insignificant in comparison with the hundreds that have already been conquered. But to win one degree low down the scale is quite a different matter from doing so at higher temperatures; in fact, to annihilate these few remaining degrees would be a far greater achievement than any so far accomplished in low temperature research. For the difficulty is twofold, having to do partly with process and partly with material. The application of the methods used in the liquefaction of gases becomes continually harder and more troublesome as the working temperature is reduced; thus, to pass from liquid air to liquid hydrogen—a difference of 60 degrees—is, from a thermodynamic point of view, as difficult as to bridge the gap of 150 degrees that separates liquid chlorine and liquid air. By the use of a new liquid gas exceeding hydrogen in volatility to the same extent as hydrogen does nitrogen, the investigator might get to within five degrees of the zero; but even a second hypothetical substance, again exceeding the first one in volatility to an equal extent, would not suffice to bring him quite to the point of his ambition. That the zero will ever be reached by man is extremely improbable. A thermometer introduced into regions outside the uttermost confines of the earth's atmosphere might approach the absolute zero, provided that its parts were highly transparent to all kinds of radiation, otherwise it would be affected by the radiation of the sun, and would therefore become heated. But supposing all difficulties to be overcome, and the experimenter to be able to reach within a few degrees of the zero, it is by no means certain that he would find the near approach of the death of matter sometimes pictured. Any forecast of the phenomena that would be seen must be based on the assumption that there is continuity between the processes studied at attainable temperatures and those which take place at still lower ones. Is such an assumption justified? It is true that many changes in the properties of substances have been found to vary steadily with the degree of cold to which they are exposed. But it would be rash to take for granted that the changes which have been traced in explored regions continue to the same extent and in the same direction in those which are as yet unexplored. Of such a breakdown low-temperature research has already yielded a direct proof at least in one case. A series of experiments with pure metals showed that their electrical resistance gradually decreases as they are cooled to lower and lower temperatures, in such ratio that it appeared probable that at the zero of absolute temperature they would have no resistance at all and would become perfect conductors of electricity. This was the inference that seemed justifiable by observations taken at depths of cold which can be obtained by means of liquid air and less powerful refrigerants. But with the advent of the more powerful refrigerant liquid hydrogen it became necessary to revise that conclusion. A discrepancy was first observed when a platinum resistance thermometer was used to ascertain the temperature of that liquid boiling under atmospheric and reduced pressure. All known liquids, when forced to evaporate quickly by being placed in the exhausted receiver of an air-pump, undergo a reduction in temperature, but when hydrogen was treated in this way it appeared to be an exception. The resistance thermometer showed no such reduction as was expected, and it became a question whether it was the hydrogen or the thermometer that was behaving abnormally. Ultimately, by the adoption of other thermometrical appliances, the temperature of the hydrogen was proved to be lowered by exhaustion as theory indicated. Hence it was the platinum thermometer which had broken down: in other words,

the electrical resistance of the metal employed in its construction was not, at temperatures about *minus* 250° C., decreased by cold in the same proportion as at temperatures about *minus* 200°. This being the case, there is no longer any reason to suppose that at the absolute zero platinum would become a perfect conductor of electricity; and in view of the similarity between the behaviour of platinum and that of other pure metals in respect of temperature and conductivity, the presumption is that the same is true of them also. At any rate, the knowledge that in the case of at least one property of matter we have succeeded in attaining a depth of cold sufficient to bring about unexpected change in the law expressing the variation of that property with temperature, is sufficient to show the necessity for extreme caution in extending our inferences regarding the properties of matter near the zero of temperature. Lord Kelvin evidently anticipates the possibility of more remarkable electrical properties being met with in the metals near the zero. A theoretical investigation on the relation of "electrons" and atoms has led him to suggest a hypothetical metal having the following remarkable properties:—Below 1 degree absolute it is a perfect insulator of electricity, at 2 degrees it shows noticeable conductivity, and at 6 degrees it possesses high conductivity. It may safely be predicted that liquid hydrogen will be the means by which many obscure problems of physics and chemistry will ultimately be solved, so that the liquefaction of the last of the old permanent gases is as pregnant now with future consequences of great scientific moment as was the liquefaction of chlorine in the early years of the last century.

The next step towards the absolute zero is to find another gas more volatile than hydrogen, and that we possess in the gas occurring in cleveite, identified by Ramsay as helium, a gas which is widely distributed, like hydrogen, in the sun, stars, and nebulae. A specimen of this gas was subjected by Olszewski to liquid air temperatures, combined with compression and subsequent expansion, following the Cailletet method, and resulted in his being unable to discover any appearance of liquefaction, even in the form of mist. His experiments led him to infer that the boiling-point of the substance is probably below 9 degrees absolute. After Lord Rayleigh had found a new source of helium in the gases which are derived from the Bath springs, and liquid hydrogen became available as a cooling agent, a specimen of helium cooled in liquid hydrogen showed the formation of fluid, but this turned out to be owing to the presence of an unknown admixture of other gases. As a matter of fact, a year before the date of this experiment I had recorded indications of the presence of unknown gases in the spectrum of helium derived from this source. When subsequently such condensable constituents were removed, the purified helium showed no signs of liquefaction, even when compressed to 80 atmospheres, while the tube containing it was surrounded with solid hydrogen. Further, on suddenly expanding, no instantaneous mist appeared. Thus helium was definitely proved to be a much more volatile substance than hydrogen in either the liquid or solid condition. The inference to be drawn from the adiabatic expansion effected under the circumstances is that helium must have touched a temperature of from 9 to 10 degrees for a short time without showing any signs of liquefaction, and consequently that the critical-point must be still lower. This would force us to anticipate that the boiling-point of the liquid will be about 5 degrees absolute, or liquid helium will be four times more volatile than liquid hydrogen, just as liquid hydrogen is four times more volatile than liquid air. Although the liquefaction of the gas is a problem for the future, this does not prevent us from safely anticipating some of the properties of the fluid body. It would be twice as dense as liquid hydrogen, with a critical pressure of only 4 or 5 atmospheres. The liquid would possess a very feeble surface tension, and its compressibility and expansibility would be about four times that of liquid hydrogen, while the heat required to vaporise the mole-

cule would be about one-fourth that of liquid hydrogen. Heating the liquid 1 degree above its boiling-point would raise the pressure by $1\frac{1}{2}$ atmospheres, which is more than four times the increment for liquid hydrogen. The liquid would be only seventeen times denser than its vapour, whereas liquid hydrogen is sixty-five times denser than the gas it gives off. Only some 3 or 4 degrees would separate the critical temperature from the boiling-point and the melting-point, whereas in liquid hydrogen the separation is respectively 10 and 15 degrees. As the liquid refractivities for oxygen, nitrogen, and hydrogen are closely proportional to the gaseous values, and as Lord Rayleigh has shown that helium has only one-fourth the refractivity of hydrogen, although it is twice as dense, we must infer that the refractivity of liquid helium would also be about one-fourth that of liquid hydrogen. Now hydrogen has the smallest refractivity of any known liquid, and yet liquid helium will have only about one-fourth of this value—comparable, in fact, with liquid hydrogen just below its critical point. This means that the liquid will be quite exceptional in its optical properties, and very difficult to see. This may be the explanation of why no mist has been seen on its adiabatic expansion from the lowest temperatures. Taking all these remarkable properties of the liquid into consideration, one is afraid to predict that we are at present able to cope with the difficulties involved in its production and collection. Provided the critical-point is, however, not below 8 degrees absolute, then from the knowledge of the conditions that are successful in producing a change of state in hydrogen through the use of liquid air, we may safely predict that helium can be liquefied by following similar methods. If, however, the critical-point is as low as 6 degrees absolute, then it would be almost hopeless to anticipate success by adopting the process that works so well with hydrogen. The present anticipation is that the gas will succumb after being subjected to this process, only, instead of liquid air under exhaustion being used as the primary cooling agent, liquid hydrogen evaporated under similar circumstances must be employed. In this case the resulting liquid would require to be collected in a vacuum vessel, the outer walls of which are immersed in liquid hydrogen. The practical difficulties and the cost of the operation will be very great; but, on the other hand, the descent to a temperature within 5 degrees of the zero would open out new vistas of scientific inquiry, which would add immensely to our knowledge of the properties of matter. To command in our laboratories a temperature which would be equivalent to that which a comet might reach at an infinite distance from the sun would indeed be a great triumph for science. If the present Royal Institution attack on helium should fail, then we must ultimately succeed by adopting a process based on the mechanical production of cold through the performance of external work. When a turbine can be worked by compressed helium, the whole of the mechanism and circuits being kept surrounded with liquid hydrogen, then we need hardly doubt that the liquefaction will be effected. In all probability gases other than helium will be discovered of greater volatility than hydrogen. It was at the British Association meeting in 1896 that I made the first suggestion of the probable existence of an unknown element which would be found to fill up the gap between argon and helium, and this anticipation was soon taken up by others and ultimately confirmed. Later, in the Bakerian Lecture for 1901, I was led to infer that another member of the helium group might exist having the atomic weight about 2, and this would give us a gas still more volatile, with which the absolute zero might be still more nearly approached. It is to be hoped that some such element or elements may yet be isolated and identified as cerium or nebulium. If amongst the unknown gases possessing a very low critical-point some have a high critical pressure, instead of a low one, which ordinary experience would lead us to anticipate, then such difficultly liquefiable gases would produce fluids having different physical properties

from any of those with which we are acquainted. Again, gases may exist having smaller atomic weights and densities than hydrogen, yet all such gases must, according to our present views of the gaseous state, be capable of liquefaction before the zero of temperature is reached. The chemists of the future will find ample scope for investigation within the apparently limited range of temperature which separates solid hydrogen from the zero. Indeed, great as is the sentimental interest attached to the liquefaction of these refractory gases, the importance of the achievement lies rather in the fact that it opens out new fields of research and enormously widens the horizon of physical science, enabling the natural philosopher to study the properties and behaviour of matter under entirely novel conditions. This department of enquiry is as yet only in its infancy, but speedy and extensive developments may be looked for, since within recent years several special cryogenic laboratories have been established for the prosecution of such researches, and a liquid-air plant is becoming a common adjunct to the equipment of the ordinary laboratory.

The Upper Air and Auroras.

The present liquid ocean, neglecting everything for the moment but the water, was at a previous period of the earth's history part of the atmosphere, and its condensation has been brought about by the gradual cooling of the earth's surface. This resulting ocean is subjected to the pressure of the remaining uncondensed gases, and as these are slightly soluble they dissolve to some extent in the fluid. The gases in solution can be taken out by distillation or by exhausting the water, and if we compare their volume with the volume of the water as steam, we should find about 1 volume of air in 60,000 volumes of steam. This would then be about the rough proportion of the relatively permanent gas to condensable gas which existed in the case of the vaporised ocean. Now let us assume the surface of the earth gradually cooled to some 200 degrees below the freezing-point; then, after all the present ocean was frozen, and the climate became three times more intense than any arctic frost, a new ocean of liquid air would appear, covering the entire surface of the frozen globe about thirty-five feet deep. We may now apply the same reasoning to the liquid air ocean that we formerly did to the water one, and this would lead us to anticipate that it might contain in solution some gases that may be far less condensable than the chief constituents of the fluid. In order to separate them we must imitate the method of taking the gases out of water. Assume a sample of liquid air cooled to the low temperature that can be reached by its own evaporation, connected by a pipe to a condenser cooled in liquid hydrogen; then any volatile gases present in solution will distil over with the first portions of the air, and can be pumped off, being uncondensable at the temperature of the condenser. In this way, a gas mixture, containing, of the known gases, free hydrogen, helium, and neon, has been separated from liquid air. It is interesting to note in passing that the relative volatilities of water and oxygen are in the same ratio as those of liquid air and hydrogen, so that the analogy between the ocean of water and that of liquid air has another suggestive parallel. The total uncondensable gas separated in this way amounts to about one fifty-thousandth of the volume of the air, which is about the same proportion as the air dissolved in water. That free hydrogen exists in air in small amount is conclusively proved, but the actual proportion found by the process is very much smaller than Gautier has estimated by the combustion method. The recent experiments of Lord Rayleigh show that Gautier, who estimated the hydrogen present as one five-thousandth, has in some way produced more hydrogen than he can manage to extract from pure air by a repetition of the same process. The spectroscopic examination of these gases throws new light upon the question of the aurora and the nature of the upper air. On passing electric discharges through the

tubes containing the most volatile of the atmospheric gases, they glow with a bright orange light, which is especially marked at the negative pole. The spectroscope shows that this light consists, in the visible part of the spectrum, chiefly of a succession of strong rays in the red, orange, and yellow, attributed to hydrogen, helium, and neon. Besides these, a vast number of rays, generally less brilliant, are distributed through the whole length of the visible spectrum. The greater part of these rays are of, as yet, unknown origin. The violet and ultra-violet part of the spectrum rivals in strength that of the red and yellow rays. As these gases probably include some of the gases that pervade interplanetary space, search was made for the prominent nebular, coronal, and auroral lines. No definite lines agreeing with the nebular spectrum could be found, but many lines occurred closely coincident with the coronal and auroral spectrum. But before discussing the spectroscopic problem it will be necessary to consider the nature and condition of the upper air.

According to the old law of Dalton, supported by the modern dynamical theory of gases, each constituent of the atmosphere while acted upon by the force of gravity forms a separate atmosphere, completely independent, except as to temperature, of the others, and the relations between the common temperature and the pressure and altitude for each specific atmosphere can be definitely expressed. If we assume the altitude and temperature known, then the pressure can be ascertained for the same height in the case of each of the gaseous constituents, and in this way the percentage composition of the atmosphere at that place may be deduced. Suppose we start with a surface atmosphere having the composition of our air, only containing two ten-thousandths of hydrogen, then at thirty-seven miles, if a sample could be procured for analysis, we believe that it would be found to contain 12 per cent of hydrogen and only 10 per cent of oxygen. The carbonic acid practically disappears; and by the time we reach forty-seven miles, where the temperature is *minus* 132 degrees, assuming a gradient of 3.2 degrees per mile, the nitrogen and oxygen have so thinned out that the only constituent of the upper air which is left is hydrogen. If the gradient of temperature were doubled, the elimination of the nitrogen and oxygen would take place by the time thirty-seven miles was reached, with a temperature of *minus* 220 degrees. The permanence of the composition of the air at the highest altitudes, as deduced from the basis of the dynamical theory of gases, has been discussed by Stoney, Bryan, and others. It would appear that there is a consensus of opinion that the rate at which gases like hydrogen and helium could escape from the earth's atmosphere would be excessively slow. Considering that to compensate any such loss the same gases are being supplied by actions taking place in the crust of the earth, we may safely regard them as necessarily permanent constituents of the upper air. The temperature at the elevations we have been discussing would not be sufficient to cause any liquefaction of the nitrogen and oxygen, the pressure being so low. If we assume the mean temperature as about the boiling-point of oxygen at atmospheric pressure, then a considerable amount of the carbonic acid must solidify as a mist, if the air from a lower level be cooled to this temperature; and the same result might take place with other gases of relatively small volatility which occur in air. This would explain the clouds that have been seen at an elevation of fifty miles, without assuming the possibility of water vapour being carried up so high. The temperature of the upper air must be above that on the vapour pressure curve corresponding to the barometric pressure at the locality, otherwise liquid condensation must take place. In other words, the temperature must be above the dew-point of air at that place. At higher elevations, on any reasonable assumption of temperature distribution, we inevitably reach a temperature where the air would condense, just as Fourier and Poisson supposed it would, unless the

temperature is arrested in some way from approaching the zero. Both ultra-violet absorption and the prevalence of electric storms may have something to do with the maintenance of a higher mean temperature. The whole mass of the air above forty miles is not more than one seven-hundredth part of the total mass of the atmosphere, so that any rain or snow of liquid or solid air, if it did occur, would necessarily be of a very tenuous description. In any case, the dense gases tend to accumulate in the lower strata, and the lighter ones to predominate at the higher altitudes, always assuming that a steady state of equilibrium has been reached. It must be observed, however, that a sample of air taken at an elevation of nine miles has shown no difference in composition from that at the ground, whereas, according to our hypothesis, the oxygen ought to have been diminished to 17 per cent, and the carbonic acid should also have become much less. This can only be explained by assuming that a large intermixture of different layers of the atmosphere is still taking place at this elevation. This is confirmed by a study of the motions of clouds about six miles high, which reveals an average velocity of the air currents of some seventy miles an hour; such violent winds must be the means of causing the intermingling of different atmospheric strata. Some clouds, however, during hot and thundery weather, have been seen to reach an elevation of seventeen miles, so that we have direct proof that on occasion the lower layers of atmosphere are carried to a great elevation. The existence of an atmosphere at more than a hundred miles above the surface of the earth is revealed to us by the appearance of meteors and fireballs, and when we can take photographs of the spectrum of such apparitions we shall learn a great deal about the composition of the upper air. In the meantime Pickering's solitary spectrum of a meteor reveals an atmosphere of hydrogen and helium, and so far this is corroborative of the doctrine we have been discussing. It has long been recognised that the aurora is the result of electric discharges within the limits of the earth's atmosphere, but it was difficult to understand why its spectrum should be so entirely different from anything which could be produced artificially by electric discharges through rarefied air at the surface of the earth. Writing in 1879, Rand Capron, after collecting all the recorded observations, was able to enumerate no more than nine auroral rays, of which but one could with any probability be identified with rays emitted by atmospheric air under an electric discharge. Vogel attributed this want of agreement between nature and experiment, in a vague way, to difference of temperature and pressure; and Zollner thought the auroral spectrum to be one of a different order, in the sense in which the line and band spectra of nitrogen are said to be of different orders. Such statements were merely confessions of ignorance. But since that time observations of the spectra of auroras have been greatly multiplied, chiefly through the Swedish and Danish Polar Expeditions, and the length of spectrum recorded on the ultra-violet side has been greatly extended by the use of photography, so that, in a recent discussion of the results, M. Henri Stassano is able to enumerate upwards of one hundred auroral rays, of which the wavelength is more or less approximately known, some of them far in the ultra-violet. Of this large number of rays he is able to identify, within the probable limits of errors of observation, about two-thirds as rays, which Professor Liveing and myself have observed to be emitted by the most volatile gases of atmospheric air unliquefiable at the temperature of liquid hydrogen. Most of the remainder he ascribes to argon, and some he might, with more probability, have identified with krypton or xenon rays, if he had been aware of the publication of wave-lengths of the spectra of those gases, and the identification of one of the highest rays of krypton with that most characteristic of auroras. The rosy tint often seen in auroras, particularly in the streamers, appears to be due mainly to neon, of which the spectrum is remarkably rich in red and orange rays. One or two neon rays are amongst those most frequently

observed, while the red ray of hydrogen and one red ray of krypton have been noticed only once. The predominance of neon is not surprising, seeing that from its relatively greater proportion in air and its low density it must tend to concentrate at higher elevations. So large a number of probable identifications warrants the belief that we may yet be able to reproduce in our laboratories the auroral spectrum in its entirety. It is true that we have still to account for the appearance of some, and the absence of other, rays of the newly discovered gases, which in the way in which we stimulate them appear to be equally brilliant, and for the absence, with one doubtful exception, of all the rays of nitrogen. If we cannot give the reason of this, it is because we do not know the mechanism of luminescence—nor even whether the particles which carry the electricity are themselves luminous, or whether they only produce stresses causing other particles which encounter them to vibrate; yet we are certain that an electric discharge in a highly rarefied mixture of gases lights one element, and not another, in a way which, to our ignorance, seems capricious. The Swedish North Polar Expedition concluded from a great number of trigonometrical measurements that the average above the ground of the base of the aurora was fifty kilometres (thirty-four miles) at Cape Thorsden, Spitzbergen; at this height the pressure of the nitrogen of the atmosphere would be only about one-tenth of a millimetre, and Moissan and Deslandres have found that in atmospheric air at pressures less than one millimetre the rays of nitrogen and oxygen fade and are replaced by those of argon and by five new rays which Stassano identifies with rays of the more volatile gases measured by us. Also Collie and Ramsay's observations on the distance to which electrical discharges of equal potential traverse different gases explosively throw much light on the question; for they find that, while for helium and neon this distance is from 250 to 300 m.m., for argon it is $45\frac{1}{2}$ m.m., for hydrogen it is 39 m.m., and for air and oxygen still less. This indicates that a good deal depends on the very constitution of the gases themselves, and certainly helps us to understand why neon and argon, which exist in the atmosphere in larger proportions than helium, krypton, or xenon, should make their appearance in the spectrum of auroras almost to the exclusion of nitrogen and oxygen. How much depends not only on the constitution and it may be temperature of the gases, but also on the character of the electric discharge, is evident from the difference between the spectra at the cathode and anode in different gases, notably in nitrogen and argon, and not less remarkably in the more volatile compounds of the atmosphere. Paulsen thinks the auroral spectrum wholly due to cathodic rays. Without stopping to discuss that question, it is certain that changes in the character of the electric discharge produce definite changes in the spectra excited by them. It has long been known that in many spectra the rays which are inconspicuous with an uncondensed electric discharge become very pronounced when a Leyden jar is in the circuit. This used to be ascribed to a higher temperature in this condensed spark, though measurements of that temperatures have not borne out the explanation. Schuster and Hemsalech have shown that these changes of spectra are in part due to the oscillatory character of the condenser discharge which may be enhanced by self-induction, and the corresponding change of spectrum thereby made more pronounced. Lightning we should expect to resemble condensed discharge much more than aurora, but this is not borne out by the spectrum. Pickering's recent analysis of the spectrum of a flash obtained by photography shows, out of nineteen lines measured by him, only two which can be assigned with probability to nitrogen and oxygen, while three hydrogen rays most likely due to water are very conspicuous, and eleven may be reasonably ascribed to argon, krypton, and xenon, one to more volatile gas of the neon class, and the brightest ray of all is but a very little less re-rangible than

the characteristic auroral ray, and coincides with a strong ray of calcium, but also lies between, and close to, an argon and a neon ray, neither of them weak rays. There may be some doubt about the identification of the spectral rays of auroras because of the wide limits of the probable errors in measuring wave-lengths so faint as most of them are, but there is no such doubt about the wave-lengths of the rays in solar protuberances measured by Deslandres and Hale. Stassano found that these rays, forty-four in number, lying between the Fraunhofer line F and 3148 in the ultra-violet, agree very closely with rays which Professor Liveing and myself measured in the spectra of the most volatile atmospheric gases. It will be remembered that one of the earliest suggestions as to the nature of solar prominences was that they were solar auroras. This supposition helped to explain the marvellous rapidity of their changes, and the apparent suspension of brilliant self-luminous clouds at enormous heights above the sun's surface. Now the identification of the rays of their spectra with those of the most volatile gases, which also furnish many of the auroral rays, certainly supports that suggestion. A stronger support, however, seems to be given to it by the results obtained at the total eclipse of May, 1901, by the American expedition to Sumatra. In the *Astrophysical Journal* for June last is a list of 339 lines in the spectrum of the corona photographed by Humphreys, during totality, with a very large concave grating. Of these no fewer than 209 do not differ from lines we have measured in the most volatile gases of the atmosphere, or in krypton or xenon, by more than one unit of wave-length on Armstrong's scale, a quantity within the limit of probable error. Of the remainder, a good many agree to a like degree with argon lines, a very few with oxygen lines, and still fewer with nitrogen lines; the characteristic green auroral ray, which is not in the range of Humphreys' photographs, also agrees within a small fraction of a unit of wave-length with one of the rays emitted by the most volatile atmospheric gas. Taking into account the Fraunhofer lines H, K, and G, usually ascribed to calcium, there remain only fifty-five lines of the 339 unaccounted for to the degree of probability indicated. Of these considerably more than half are very weak lines which have not depicted themselves on more than one of the six films exposed, and extend but a very short distance into the sun's atmosphere. There are, however, seven which are stronger lines, and reach to a considerable height above the sun's rim, and all have depicted themselves on at least four of the six films. If there be no considerable error in the wave-lengths assigned (and such is not likely to be the case), these lines may perhaps be due to some volatile element which may yet be discovered in our atmosphere. However that may be, the very great number of close coincidences between the auroral rays and those which are emitted under electric excitement by gases of our atmosphere almost constrains us to believe, what is indeed most probable on other grounds, that the sun's coronal atmosphere is composed of the same substances as the earth's, and that it is rendered luminous in the same way—namely, by electric discharges. This conclusion has plainly an important bearing on the explanation which should be given of the outburst of new stars and of the extraordinary and rapid changes in their spectra. Moreover, leaving on one side the question whether gases ever become luminous by the direct action of heat, apart from such transfers of energy as occurred in chemical change and electric disturbance, it demands a revision of the theories which attribute more permanent differences between the spectra of different stars to differences of temperature, and a fuller consideration of the question whether they cannot with better reason be explained by differences in the electric conditions which prevail in the stellar atmosphere.

If we turn to the question what is the cause of the electric discharges which are generally believed to occasion auroras, but of which little more has hitherto been known than that they are connected with sun-spots

and solar eruptions, recent studies of electric discharges in high vacua, with which the names of Crookes, Röntgen, Lenard, and J. J. Thomson will always be associated, have opened the way for Arrhenius to suggest a definite and rational answer. He points out that the frequent disturbances which we know to occur in the sun must cause electric discharges in the sun's atmosphere far exceeding any that occur in that of the earth. These will be attended with an ionisation of the gases, and the negative ions will stream away through the outer atmosphere of the sun into the interplanetary space, becoming, as Wilson has shown, nuclei of aggregation of condensable vapours and cosmic dust. The liquid and solid particles thus formed will be of various sizes; the larger will gravitate back to the sun, while those with diameters less than one and a half thousandths of a millimetre, but nevertheless greater than a wave-length of light, will, in accordance with Clerk-Maxwell's electromagnetic theory, be driven away from the sun by the incidence of the solar rays upon them, with velocities which may become enormous, until they meet other celestial bodies, or increase their dimensions by picking up more cosmic dust or diminish them by evaporation. The earth will catch its share of such particles on the side which is turned towards the sun, and its upper atmosphere will thereby become negatively electrified until the potential of the charge reaches such a point that a discharge occurs, which will be repeated as more charged particles reach the earth. This theory not only accounts for the auroral discharges, and the coincidence of their times of greatest frequency with those of the maxima of sunspots, but also for the minor maxima and minima. The vernal and autumnal maxima occur when the line through the earth and sun has its greatest inclination to the solar equator, so that the earth is more directly exposed to the region of maximum of sun-spots, while the twenty-six days period corresponds closely with the period of rotation of that part of the solar surface where faculae are most abundant. J. J. Thomson has pointed out, as a consequence of the Richardson observations, that negative ions will be constantly streaming from the sun merely regarded as a hot body, but this is not inconsistent with the supposition that there will be an excess of this emission in eruptions, and from the regions of faculae. Arrhenius' theory accounts also, in a way which seems the most satisfactory hitherto enunciated, for the appearances presented by comets. The solid parts of these objects absorb the sun's rays, and as they approach the sun become heated on the side turned towards him until the volatile substances frozen in or upon them are evaporated and diffused in the gaseous state in surrounding space, where they get cooled to the temperature of liquefaction and aggregated in drops about the negative ions. The larger of these drops gravitate towards the sun and form clouds of the coma about the head, while the smaller are driven by the incidence of the sun's light upon them away from the sun and form the tail. The curvature of the tail depends, as Bredichin has shown, on the rate at which the particles are driven, which in turn depends on the size and specific gravity of the particles, and these will vary with the density of the vapour from which they are formed and the frequency of the negative ions which collect them. In any case Arrhenius' theory is a most suggestive one, not only with reference to auroras and comets, and the solar corona and chromosphere, but also as to the constitution of the photosphere itself.

Various Low Temperature Researches.

We may now summarise some of the results which have already been attained by low-temperature studies. In the first place, the great majority of chemical interactions are entirely suspended, but an element of such exceptional powers of combination as fluorine is still active at the temperature of liquid air. Whether solid fluorine and liquid hydrogen would interact no one can at present say.

Bodies naturally become denser, but even a highly expansive substance like ice does not appear to reach the density of water at the lowest temperature. This is confirmatory of the view that the particles of matter under such conditions are not packed in the closest possible way. The force of cohesion is greatly increased at low temperatures, as is shown by the additional stress required to rupture metallic wires. This fact is of interest in connection with two conflicting theories of matter. Lord Kelvin's view is that the forces that hold together the particles of bodies may be accounted for without assuming any other agency than gravitation or any other law than the Newtonian. An opposite view is that the phenomena of the aggregation of molecules depend upon the molecular vibration as a physical cause. Hence, at the zero of absolute temperature, this vibrating energy being in complete abeyance, the phenomena of cohesion should cease to exist, and matter generally be reduced to an incoherent heap of cosmic dust. This second view receives no support from experiment.

The photographic action of light is diminished at the temperature of liquid air to about 20 per cent of its ordinary efficiency, and at the still lower temperature of liquid hydrogen only about 10 per cent of the original sensitivity remains. At the temperature of liquid air or liquid hydrogen a large range of organic bodies and many inorganic ones acquire under exposure to violet light the property of phosphorescence. Such bodies glow faintly so long as they are kept cold, but become exceedingly brilliant during the period when the temperature is rising. Even solid air is a phosphorescent body. All the alkaline earth sulphides which phosphoresce brilliantly at the ordinary temperature lose this property when cooled, to be revived on heating; but such bodies in the first instance may be stimulated through the absorption of light at the lowest temperatures. Radio-active bodies, on the other hand, like radium, which are naturally self-luminous, maintain this luminosity unimpaired at the very lowest temperatures, and are still capable of inducing phosphorescence in bodies like the platino-cyanides. Some crystals become for a time self-luminous when cooled in liquid air or hydrogen, owing to the induced electric stimulation causing discharges between the crystal molecules. This phenomenon is very pronounced with nitrate of uranium and some platino-cyanides.

In conjunction with Professor Fleming, a long series of experiments was made on the electric and magnetic properties of bodies at low temperatures. The subjects that have been under investigation may be classified as follows:—The Thermo-electric Powers of Pure Metals; the Magnetic Properties of Iron and Steel; Dielectric Constants; the Magnetic and Electric Constants of Liquid Oxygen; Magnetic Susceptibility.

The investigations have shown that electric conductivity in pure metals varies almost inversely as the absolute temperature down to *minus* 200 degrees, but that this law is greatly affected by the presence of the most minute amount of impurity. Hence the results amount to a proof that electric resistance in pure metals is closely dependent upon the molecular or atomic motion which gives rise to temperature, and that the process by which the energy constituting what is called an electric current is dissipated essentially depends upon non-homogeneity of structure and upon the absolute temperature of the material. It might be inferred that at the zero of absolute temperature resistance would vanish altogether, and all pure metals become perfect conductors of electricity. This conclusion, however, has been rendered very doubtful by subsequent observations made at still lower temperatures, which appear to point to an ultimate finite resistance. Thus the temperature at which copper was assumed to have no resistance was *minus* 223 degrees, but that metal has been cooled to *minus* 253 degrees without getting rid of all resistance. The reduction in resistance of some of the metals at the boiling-point of hydrogen is very remarkable. Thus copper has only 1 per cent, gold and platinum

3 per cent, and silver 4 per cent of the resistance they possessed at zero C., but iron still retains 12 per cent of its initial resistance. In the case of alloys and impure metals, cold brings about a much smaller decrease in resistivity, and in the case of carbon and insulators like gutta-percha, glass, ebonite, &c., their resistivity steadily increases. The enormous increase in resistance of bismuth when transversely magnetised and cooled was also discovered in the course of these experiments. The study of dielectric constants at low temperatures has resulted in the discovery of some interesting facts. A fundamental deduction from Maxwell's theory is that the square of the refractive index of a body should be the same number as its dielectric constant. So far, however, from this being the case generally, the exceptions are far more numerous than the coincidences. It has been shown in the case of many substances, such as ice and glass, that an increase in the frequency of the alternating electro-motive force results in a reduction of the dielectric constant to a value more consistent with Maxwell's law. By experiments upon many substances it is shown that even a moderate increase of frequency brings the large dielectric constant to values quite near to that required by Maxwell's law. It was thus shown that low temperature has the same effect as high frequency in annulling the abnormal dielectric values. The exact measurement of the dielectric constant of liquid oxygen, as well as its magnetic permeability, combined with the optical determination of the refractive index, showed that liquid oxygen strictly obeys Maxwell's electro-optic law even at very low electric frequencies. In magnetic work the result of greatest value is the proof that magnetic susceptibility varies inversely as the absolute temperature. This shows that the magnetisation of paramagnetic bodies is an affair of orientation of molecules, and it suggests that at the absolute zero all the feebly paramagnetic bodies will be strongly magnetic. The diamagnetism of bismuth was found to be increased at low temperatures. The magnetic moment of a steel magnet is temporarily increased by cooling in liquid air, but the increase seems to have reached a limit, because on further cooling to the temperature of liquid hydrogen hardly any further change was observed. The study of the thermo-electric relations of the metals at low temperatures resulted in a great extension of the well-known Tait Thermo-electric Diagram. Tait found that the thermo-electric power of the metals could be expressed by a linear function of the absolute temperature, but at the extreme range of temperature now under consideration this law was found not to hold generally; and, further, it appeared that many abrupt electric changes take place, which originate probably from specific molecular changes occurring in the metal. The thermo-electric neutral points of certain metals, such as lead and gold, which are located about or below the boiling-point of hydrogen, have been found to be a convenient means of defining specific temperatures in this exceptional part of the scale.

The effect of cold upon the life of living organisms is a matter of great intrinsic interest, as well as of wide theoretical importance. Experiment indicates that moderately high temperatures are much more fatal, at least to the lower forms of life, than are exceedingly low ones. Professor McKendrick froze for an hour at a temperature of -182°C . samples of meat, milk, &c., in sealed tubes; when these were opened after being kept at blood heat for a few days, their contents were found to be quite putrid. More recently, some more elaborate tests were carried out at the Jenner Institute of Preventive Medicine on a series of typical bacteria. These were exposed to the temperature of liquid air for twenty hours, but their vitality was not affected, their functional activities remained unimpaired, and the cultures which they yielded were normal in every respect. The same result was obtained when liquid hydrogen was substituted for air. A similar persistence of life in seeds has been demonstrated even at the lowest temperatures; they were frozen for over a hundred hours

in liquid air, at the instance of Messrs. Brown and Escombe, with no other result than to affect their protoplasm with a certain inertness, from which it recovered with warmth. Subsequently, commercial samples of barley, pea, vegetable-marrow, and mustard seeds were literally steeped for six hours in liquid hydrogen at the Royal Institution, yet when they were sown by Sir W. T. Thiselton Dyer at Kew in the ordinary way, the proportion in which germination occurred was no less than in the other batches of the same seeds which had suffered no abnormal treatment. Bacteria are minute vegetable cells, the standard of measurement for which is the "mikron." Yet it has been found possible to completely triturate these microscopic cells, when the operation is carried out at the temperature of liquid air, the cells then being frozen into hard breakable masses. The typhoid organism has been treated in this way, and the cell plasma obtained for the purpose of studying its toxic and immunising properties. It would hardly have been anticipated that liquid air should find such immediate application in biological research. A research by Professor Macfadyen, just concluded, has shown that many varieties of micro-organisms can be exposed to the temperature of liquid air for a period of six months without any appreciable loss of vitality, although at such a temperature the ordinary chemical processes of the cell must cease. At such a temperature the cells cannot be said to be either alive or dead, in the ordinary acceptance of these words. It is a new and hitherto unobtained condition of living matter—a third state. A final instance of the application of the above methods may be given. Certain species of bacteria during the course of their vital processes are capable of emitting light. If, however, the cells be broken up at the temperature of liquid air, and the crushed contents brought to the ordinary temperature, the luminosity function is found to have disappeared. This points to the luminosity not being due to the action of a ferment—a "Luciferase"—but as being essentially bound up with the vital processes of the cells, and dependent for its production on the intact organisation of the cell. These attempts to study by frigorific methods the physiology of the cell have already yielded valuable and encouraging results, and it is to be hoped that this line of investigation will continue to be vigorously prosecuted at the Jenner Institute.

And now, to conclude an Address which must have sorely taxed your patience, I may remind you that I commenced by referring to the plaint of Elizabethan science, that cold was not a natural available product. In the course of a long struggle with nature, man, by the application of intelligent and steady industry, has acquired a control over this agency which enables him to produce it at will, and with almost any degree of intensity, short of a limit defined by the very nature of things. But the success in working what appears, at first sight, to be a quarry of research that would soon suffer exhaustion, has only brought him to the threshold of new labyrinths, the entanglements of which frustrate, with a seemingly invulnerable complexity, the hopes of further progress. In a legitimate sense all genuine scientific workers feel that they are "the inheritors of unfulfilled renown." The battlefields of science are the centres of a perpetual warfare, in which there is no hope of final victory, although partial conquest is ever triumphantly encouraging the continuance of the disciplined and strenuous attack on the seemingly impregnable fortress of Nature. To serve in the scientific army, to have shown some initiative, and to be rewarded by the consciousness that in the eyes of his comrades he bears the accredited accolade of successful endeavour, is enough to satisfy the legitimate ambition of every earnest student of Nature. The real warranty that the march of progress in the future will be as glorious as in the past lies in the perpetual reinforcement of the scientific ranks by recruits animated by such a spirit, and proud to obtain such a reward.

ADDRESS TO THE CHEMICAL SECTION
OF THE
BRITISH ASSOCIATION.
BELFAST, 1902.

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President of the Section.

(Continued from p. 147).

THE contention that chemical equality must be regarded as of as clearly defined a nature as gravimetric equality becomes the more weighty when it is reflected that our very definite views concerning gravimetric equality are due solely to the law of conservation of mass, the evidence for and against which, I may remind you, is just now to be discussed by Lord Rayleigh before the Physical Section. The mass of one pound of sodium remains unchanged when the metal is converted into salt, washing soda, or borax; if this were not the case, gravimetric equality would be just as definite as it is now, but physicists would have to argue for its general recognition in much the same way as I am doing now for the recognition of chemical equality.

In further justification of this claim of chemical equality to co ordinate rank with dynamical equality in the quantification of substances it may be well to take the fact into consideration that the determination of the former is independent of that of the latter. Overlooking the difficulties of the task, let there be at hand or always procurable unlimited numbers of parcels of the different substances to be experimented upon, each of which, by other means than weighing, such as spatial measurement, can be known to be equal to, or greater or less than, other parcels of the same substances. Suppose, now, that after many trials, one of a number of equal portions of sodium hydroxide has been found to be the quantity just necessary to interact with one of a number of portions of hydrochloric acid also equal among themselves. The products of the interaction will be some water and some salt. We can now have placed before us a parcel of sodium hydroxide equal to that previously used, another of hydrochloric acid, also equal to that used, and the water and the salt obtained, and then have before us chemically equal quantities of four substances. Let now, by spatial measurement, a number of parcels of water be portioned out, all equal to that of the water obtained, and a number of parcels of salt equal to that of the salt obtained. By a series of trials we find a quantity of silver nitrate just sufficient to interact with sodium chloride, and having, by supposition, taken this quantity of silver nitrate from a lot of other parcels equal to it, we find that one of these is just sufficient to interact with one of the portions of hydrochloric acid equal to that used in producing one of the portions of salt. Further, we find that the salt and the hydrochloric acid each produce a substance which is the same, namely, silver chloride, and in the same quantity as the other. Along with it in the case of the salt, is sodium nitrate, and in the case of the hydrochloric acid, nitric acid. We can then find that this quantity of nitric acid is just enough to interact with one of those of sodium hydroxide, and thereby produce quantities of sodium nitrate and water, respectively equal to those obtained in the other interactions. If now we conjoin with these experiments others in which hydrogen, sodium, and silver are each caused to combine with chlorine, and others in which hydrochloric acid, silver chloride, and sodium chloride are electrolysed into these elementary substances, evidence is obtained of such facts of chemical composition and decomposition and of double decomposition (or what happens when compounds interact) as those upon which the science of chemistry is framed.

In teaching chemistry the point is kept too much in the background, if not altogether out of sight, that the chemical equality of quantities of different substances is

independent of all other relations of equality between them, and that, therefore, its validity is not affected by the fact of its terms agreeing with some and not with other terms of equalities determined in other ways. Instead of bringing out this point the molecule of water is given out as being, primarily and prominently, that quantity which has eighteen units of mass, and which measures two unit volumes. Both statements happen in the nature of things to be true, but neither of them describes the molecule. Let it be clearly understood from illustrative examples what is meant by "chemically equal," and there is hardly more to be said as to what constitutes a molecule of water than that it is the quantity of it chemically equal to that of some other substance presenting itself for comparison. "Molecule" is a term of relation: it stands for an equal quantity, not for any particular quantity; but as such it is as easy to understand and as indefinable as an equal volume or an equal weight of a substance.

It is then only as colligated equalities, established by experiment, that gaseous volumes, osmotic pressures, and other properties of substances come into consideration, first as enforcing the truth of the conception of the indicated quantities as equal, and then as the means of molecular measurement without resort to chemical change. But of the purposes served by the colligative properties, that of giving molecular measurements without recourse to the evidence afforded by chemical change is well known to be of the very widest application. To determine chemically the molecular equalities of substances, single chemical changes of suitable character, changes which are cases of double decomposition, have to be looked for; and to know these with the desirable degree of certainty calls for a much larger acquaintance with the chemical behaviour of the substances than can usually be gained at the early stage of work when the knowledge of the molecule is of the utmost assistance in the further investigation of the nature of the substances. Consequently, it is nearly always through recourse to physical methods that the molecule is first ascertained, and then through the molecule the certainty acquired that some particular interaction is a single one, thus reversing the normal order of things, which undoubtedly is that the molecule in chemistry, however it may have been first determined, is recognised as such by being what it is in chemical change.

I shall have been wholly misunderstood by you if you suppose that I would make light of the importance of the balance in chemical operations, or of the value of its indications in chemical investigations. Once the weights of molecular or atomic quantities have been ascertained, the balance becomes the most accurate and generally the most easily applied instrument for apportioning substances in these quantities. Chemical interaction, to be employed in this way and without the aid of the balance, is practically useless, for the reason that it involves the destruction of the quantities it measures. Out of this dependence on the balance arises the exceeding importance of accurate tables of atomic weights, from which molecular weights are derived by addition; but the place for these tables is not on the walls of the lecture-theatre, but in the laboratory pocket-book, and, perhaps, in the balance-room. Besides the use of the balance and of atomic weight tables for getting and calculating out molecules of different substances at pleasure, there is the indispensable service they perform in enabling chemical analysis to be carried out and applied to the solution of the problems offered by chemical change. The primary problem of every science is to find some element of sameness in the diversity of its phenomena, in order that they may be compared, a problem which was solved for chemistry to a large extent by Dalton, and ceased to exist when the distinction had been made between molecule and atom. But this having been solved, there comes the other problem, namely, to find definite, that is, quantitative differences in the midst of the uniformities,

and these for the chemist are differences of mass or weight. Through that redistribution of mass which attends chemical interactions it has been possible to trace out to some extent the nature of the transformation of substances and develop the science on the lines of chemical composition and chemical constitution. Thus, then, the balance has become and will continue to be the necessary instrument of chemical research; but again I would remind you that it records its facts in units which are not ours, and of which we avail ourselves only as the means to an end. Sodium chloride is chemically composed, not of 3545 equal parts of chlorine with 2305 of the same equal parts of sodium, but of equal quantities of these simple substances.

The theory of chemical molecules or equalities and their relations to the equalities between the weights and gaseous volumes of different substances were brought to light not by Richter's law of chemical combining proportions, and not by Avogadro's hypothesis as to their being equal numbers of particles in the same volume of different gases, but in the first place by Dalton's atomic theory and Gay-Lussac's law of simply related gaseous volumes in chemical change; and then, much more fully in the middle of the last century, through the brilliant work of Gerhardt, Williamson, Laurent, Odling, Wurtz, and others, in the purely chemical field. Dalton gave us the conception of the molecule, though confused with that of the atom, as the unit of measure of chemical activity in place of the gravimetric unit; the work of the chemists of the last mid-century gave us a fuller conception of the molecule, along with the notion of chemical change as being substitution in the molecule effected by what became known as double decomposition. Up to that time chemistry had been treated only as the science of compounding and decomposing or reducing. Sodium added to oxygen gives soda, sulphur added to oxygen gives sulphuric anhydride, soda added to the anhydride gives sodium sulphate, ethylene added to chlorine gives dichlorethane, water subtracted from alcohol leaves ether, and so forth. All this is strictly true in a limited way, but then it is not chemistry; and the addition precedes and does not constitute the chemical union. In the sodium sulphate we perceive no soda, no anhydride, no sodium, sulphur, or oxygen. That is to say, there is evidence of the addition and subtraction of mass and some other such evidence; but, for the rest, evidence of addition there is none. Were it otherwise there could be no chemistry. It is true that one of the great things accomplished by chemistry has been that of establishing the law of the conservation of mass, without which to rely upon the chemist would be unable to carry on his experimental investigations. But that is only because, like the steady point to the seismologist, it is there unchangeable when all else is changing. Since it is the law of no change, it cannot serve to explain what is change. Far from being the science of the composition of substances, chemistry might be defined as being the science of the non-composition of substances where that composition might have been looked for from the antecedents. If salt is verily a compound of sodium and chlorine, and can be broken up into these, why have the fragments not the marks on them of that whole of which they formed a part? It is true that 5850 parts of salt become 3545 parts of chlorine and 2305 parts of sodium, nothing being gained or lost in weight; but to account for that there is no need of chemistry, a science which takes cognisance of the phenomena of change, and not of those of unchanged properties. The use of the word "composition" in chemistry cannot be discarded now, and all that is necessary to make it unobjectionable is to see that the term is always qualified by the prefix "chemical" when there is a possibility of mistake about its significance, and that that significance is carefully explained, if not defined and fully illustrated, before it is given over to the beginner.

The facts of a chemical nature about common salt which

cause the statement to be made that it is a chemical compound of chlorine and sodium are such as these. Salt can be wholly changed into sodium and chlorine; these substances brought together change into salt and nothing else; salt and sodium, each under conditions appropriate to it, change into the same substance, called also a sodium compound, such as sodium hydroxide; salt and chlorine, each in its own way, change into the same chlorine compound, such as hydrochloric acid; neither sodium nor chlorine, one apart from the other or the other's chemical compounds, ever changes into salt; salt is, directly or indirectly, producible in the chemical interaction of a sodium compound with a chlorine compound; the properties of salt are much less like those of either sodium or chlorine than like those of some other substances; in sensible and other physical properties the chemically compound substance, salt, is as simple as or simpler than either of the chemically simple substances, sodium and chlorine; lastly, the laws of combining proportion by weight are obeyed in all the chemical changes in which salt takes part.

With exclusive reference to such facts as these, the chemical composition of a substance will, I think, be found to be satisfactorily defined, as its having the power, capacity, or property of being wholly producible from and wholly convertible into, directly or indirectly, those substances of which it is said to be composed. A simple substance differs from one that is compound only in not possessing the power of being by itself convertible into two others, or of being produced alone from any two others. Simple substances are not less varied or less complex in their physical properties than compound substances, while their chemical constitution is often more problematic than that of many which are compound. The term "simple," therefore, is as misleading in the language of chemistry as "compound," unless defined and qualified in use by the word "chemically."

The ground really occupied by chemical composition in theoretical chemistry is now greatly limited; for with the full acceptance of the idea of the molecule and of the atom as a derivative of it, its place has been taken by chemical constitution to an extent hardly realised. The useful and practically necessary expression of the results of the quantitative analysis of a new substance gravimetrically is all that can strictly receive the name of its chemical composition. When the term is applied more widely it is used for what are really the simpler forms of chemical constitution. It was otherwise before the conception of the molecule had become current and the atom had become a derived function of the molecule. Chemical composition as expressed by Dalton in atoms is indeed that and nothing else. Carbonic anhydride is composed, according to him, of two atoms of oxygen to one of carbon, as against carbonic oxide which is composed of one; marsh gas of two atoms of hydrogen to one of carbon, as against olefiant gas composed of one. But then it was only numerical necessity which led him to adopt such a mode of expressing the facts. The same necessity, it is true, affects us also in the matter of carbon dioxide, of water, and of ammonia, but how little it does so is shown by the many cases in which the empirical or simple composition is expressed in multiples. The atomic chemical composition of ethylene is two of hydrogen to one of carbon, and that of benzene one of hydrogen to one of carbon. When we say, as we always do, that the one substance is "composed" of four atoms of hydrogen to two of carbon, and the other of six of hydrogen to six of carbon, we give what is information concerning the constitution of these substances. Call it the composition of the molecule as we may, it is evident that by composition we can here mean only constitution. As with polymerism, so with isomerism, and in a more marked way. Mercurous sulphate and mercuric oxysulphate, quite distinct salts, have yet the same composition.

In the great reformation wrought by the chemists to

whom I have referred, but by Gerhardt in particular, the new light set up in chemistry was the notion of what came to be called "double decomposition" in chemical change. The phrase is not, perhaps, happily constructed, but it has the merit of needing some explanation of its meaning before it can be understood, and troubles, therefore, through a too simple apprehension of the sense of the word "composition" are hardly to be feared. Its introduction into chemistry marked the ascendancy of the idea of the molecule as the factor in chemical change whose interactions with other molecules were to be considered, instead of those additions which, as chemical phenomena, never take place. It led also to new conceptions of the nature of the atom and the compound radical as being the quantitative and qualitative expressions of the powers possessed by substances to change into others, and to the conception of the valency of atoms and radicals as expressing the nature of the connection of successive chemical changes. The zeal with which it was attempted to force all chemical changes into the form of double decomposition interfered, perhaps, with the full recognition of its importance; but the fact remains that, with hardly an exception, all that is stated concerning the nature of those chemical changes in which two or three substances become one, or one becomes two or more, is based upon notions derived from the study of double decomposition.

The fundamental value of double decomposition consists in its displaying threads running through chemical transformations which can be followed up. When two substances change into two others, and only then, there can be found, in most cases relations of resemblance, both physical and chemical, between the before and after of a chemical change. Instead of the striking likenesses shown by the substances formed by quasi-addition to those from which they are formed, there are here met with the similarities of the outcoming to the interacting substances, and the similarities between the products of different interactions in which the acting substances are similar. Chemists had been for very long familiar with acids, bases, salts, without becoming deeply impressed with the significance of the resemblances which these class-names imply, and also with the facts that acids beget acids, bases bases, and salts salts, or in more general terms, that substances in interaction produce others like them, and that differences between the products and the agents in one change are distinctly repeated in a similar change in which other substances are concerned, points now given expression to by such terms as "chemical constitution," "homologous," and "analogous series," "Kopp's law," &c.

What is so important to consider in the study of double decomposition is that the fact, that the sum of the masses of the two products of the change is the sum of the masses of the two interacting substances, presents itself no longer as being merely the evidence of the massing together of substances into a compound; for there is in double decomposition to be considered that redistribution of mass which, on the one hand, is found to correspond to, and be part of, a general though not sharply defined re-distribution of physical and chemical properties; and, on the other hand, to be obviously irreducible to that interchange of those simpler substances which in many cases are produced in the simple decomposition of the acting substances.

The physical properties of substances, or rather their sensible qualities, are of too uncertain a character for their redistribution to be safely traced. But it generally does result, amongst inorganic substances, at least, that colour is transmitted, the saline, acid, bitter, or other taste of one of the active substances will appear, with more or less distinctness, in one of the products, a relatively volatile and a relatively fixed substance together will yield a similar pair of products, a dense and a light substance will yield a dense and a light substance, and so on. The chemical properties, however, are quite definitely re-

distributed to a large extent, a fact sufficiently illustrated by saying that an iron salt yields an iron salt, and a sulphate yields a sulphate.

But this is not a redistribution in which simpler substances, or indeed any other substances than those interacting, play a part; as soon becomes evident on attempting to establish the contrary by an appeal to the facts. While silver acetate and silver sulphate resemble each other and also silver nitrate as silver salts, they do not resemble silver itself; and though silver nitrate resembles sodium nitrate as nitrate, there is not even a substance known which is related to these salts as silver is related to silver salts. It might be objected to this that there may yet become known such a substance, which in its ultimate decomposition would give one molecule of nitrogen to three molecules of oxygen. If instead of nitrate were given acetate or cyanide, there would be found in the substances acetic peroxide and cyanogen, it might be said, the analogues of the as yet unknown substance of the nitrate. But the point I would make is, that nitrate, sulphate, &c., are names with well-defined meanings independent of the fact that the corresponding substances are not known; for it follows without argument that also the terms silver, iron, chloride, &c., should be equally independent in meaning of the existence of the substances silver, sodium, chlorine, &c. It is a familiar historical fact that caesium, helium, and fluorine were chemical names long before the substances caesium, helium, and fluorine became known. We might well be convinced, therefore, without going further, that constitutional names, names which convey the facts of likenesses preserved in chemical change, cannot be indicators of the presence of the substances for which they may be also used. For, that being the case, we have no grounds for assuming that silver nitrate in interaction with sodium sulphate decomposes into the substance silver, which then combines to form silver sulphate. But fuller proof than any appearance of likeness or unlikeness can give is afforded by facts which became known and appreciated in connection with the chemical molecule. Typical of them all is the fact that in none of its interactions does chloromethane yield a hydrocarbon simpler than methane or than itself. Under those conditions in which it might have been expected to give a substance which would be methyl, it produces ethane, a substance which chlorine converts into another substance, having instead of one-third only one-sixth less hydrogen in its composition. Similar results have been obtained in all cases where the point can be determined—that is, where the simpler substance looked for would still be a compound substance, and such simpler derivatives are looked for no longer. The monohydride of oxygen or sulphur, the dihydride of nitrogen or phosphorus or arsenic, the mononitride of carbon, the organic compounds, methyl, phenyl, acetyl, are not only unknown, but are held to be non-existent substances, though their chemical compounds, the hydroxides, amides, cyanides, and the rest, are both numerous and well-defined. Whatever other view we shall have to take of the constitution of Gomberg's remarkable "triphenylmethyl," it will certainly not be that it is identical with the radical of the triphenylchloromethane from which it is derived, unless we are prepared to allow that carbon is sometimes tervalent. Ethylene the substance differs from ethylene the radical in having its two carbons differently related; but it is difficult to see how to make a similar distinction in the case of Gomberg's substance.

In those other cases in which the point is not strictly determinable, only because the resulting substances are the simple substances themselves, it required but the recognition of molecular quantities to make it evident that these cases run parallel with the others. For, in all changes which can be satisfactorily followed out, the resulting or entering quantity of the simple substance is twice as great as that which can have come from, or gone to form the molecule of either of the compound sub-

stances. But if, so far as can be traced, a simple substance comes only half from one molecule of any of its compounds, none of these compounds can contain or be composed of simple substances. All simple substances, therefore, as well as all compound substances, enter into, and come out from chemical changes as dual in all of them in origin and disappearance. Their colligative properties have been appealed to in order to confirm this observation, but with conflicting results, sometimes confirmatory of the chemical evidence, sometimes contradictory of it, and sometimes too complex for confident chemical interpretation.

I refer here more especially to Avogadro's proposition, which is in effect that equal volumes of gases are chemically equal or molecular. As in the case of Dalton's atomic theory, there is to be distinguished in this proposition what Avogadro really put forward as new from what he took for granted. Admitting, as was to him a matter of course, that gases have in equal volumes equal numbers of particles, he asserted that in the case of elementary substances these particles, are not the atomic particles, but, as in the case of compound substances, particles compounded of these, which interact with the particles of other gases as chemically equal each to each. If now this proposition is divested of all hypothesis, all reference to the mechanical structure of gases, it becomes the law that equal volumes of gases at the same temperature and pressure, whether simple or compound, are almost exactly chemically equal quantities, and once in possession of this law we find nothing becomes clearer by assuming that equal volumes of different gases contain the same number of chemically equal particles. This law is, obviously, an advance upon Gay-Lussac's law similar to that of the chemical molecular theory upon the atomic theory of Dalton. Unfortunately, however, it does not hold good in the case of not a few simple substances, and it seems impossible from the chemical point of view, and consistently with the molecular theory, to admit that, because the gas-volume has only half the expected mass, the chemical molecule of sodium or mercury is not bipartite like that of hydrogen or oxygen, and chemically equal to either.

The dual constitution or chemically compound nature of the simple substances as thus established by the part they take in chemical interactions furnishes further evidence of the untenability of the belief that the molecule is chemically composed of two substances, or their substitutes, simpler than itself, when we consider that, were this true, there would be chemical union between two things perfectly alike, two portions of the same thing. This difficulty was, I believe, first raised by Berzelius, and has never been met. Physically, the matter is simple enough, if motion in the opposite direction is not counted as a difference between two masses. But this would be a non-elective union, whilst chemical union is elective.

The difficulty, insurmountable when made, does not arise when the fact is recognised that every chemically single substance, whether simple or compound, is, as a substance, one and without parts, and can never, therefore, be built up of or broken down into parts different from itself. One substance (as two molecules) or two substances change into two others or into two molecules of one, in an interaction which is instant, uninterrupted, and irresolvable into stages, where the interaction is single in character. But just as a body can be mentally analysed (as in the investigations of dynamics) into mass and motion, which apart are unknown, and as these again can each be conceived of as further divided, resolved, condensed, and otherwise qualified as centres of mass, compounded motions, and so forth, so the chemist is enabled mentally to find quantitatively defined this, that, and the other mark of the many chemical interactions which have or may have gone to bring it into existence, and will or may again have place in the possible forms of its dissolution into others. The two methyls in the constitution of ethane, about which we are quite certain, are not

two things held together till some interaction sunders them in the chemical dissolution of ethane, but the double mark of similarity between it and other methyl compounds in their chemical interactions. We cannot say that only one part of the ethane is methyl, or hydrogen, or carbon, but that part of its nature, of its constitution, is its behaviour as a methyl compound, or, again, as an ethyl compound; or, more comprehensively but less specifically, part of its constitution is its behaviour as a hydrocarbon, as a hydrogen, and as a carbon compound. But these are different aspects of it, different relations of it, not differing parts of the one homogeneous substance.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, September 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 192 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 192 samples examined by us chemically during the month, all were found to be clear, bright, and well filtered.

The rainfall at Oxford still shows a deficit, but has been fairly well distributed throughout the month, rain having fallen on twenty days. The total fall was 2.20 inches, and the average is 2.38 inches; this leaves a deficit of 0.18 inch, which, added to the previous one of 5.17 inches, makes a total deficit of 5.35 inches, or 34.1 per cent on the thirty-five years' average.

Our bacteriological examinations of 499 samples have given the results recorded in the following table; we have also examined 36 other samples, from special standpipes, wells, &c., making a total of 535 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 24 samples) ..	304
New River, filtered (mean of 126 samples) ..	13
Thames, unfiltered (mean of 24 samples) ..	5134
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 269 samples) ..	21
Ditto ditto highest	193
Ditto ditto lowest	0
River Lea, unfiltered (mean of 24 samples) ..	233
River Lea, from the East London Company's clear-water wells (mean of 32 samples) ..	33

Of the 427 samples taken daily from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, eighteen samples, or 4.2 per cent, were sterile. Three samples contained more than 150 mi-

crobes, while only twelve samples, or 2·8 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the twelve excess samples was 142, against a corresponding mean of 149 in twelve samples during July. These figures show that the Metropolitan waters are keeping well up to their usual high standard of the summer supply.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

CORKS VERSUS RUBBER.

By T. H. PAGE, B.Sc.

As it is well known to those who work with essential oils, the terpenes, especially when hot, very rapidly attack rubber corks, making them first swell and then become very soft and sticky. This is most objectionable, not only because they are disagreeable to handle, but they leave rubber on the necks of the flasks, &c., and it will often get into the distillation flask and even into the condenser tube, discolouring and spoiling the distillate.

Having had occasion to carry out a lengthy fractionation of terpenes under reduced pressure with a Young's dephlegmator, I found it practically impossible to use rubber stoppers, as they were not only in contact with the hottest vapours, but sometimes even with the liquid itself, and would have to be frequently renewed.

To overcome these difficulties I find an ordinary cork covered with gum an excellent substitute. The gum used is the ordinary gum mullage, but rather thick. It is conveniently applied with a brush. The apparatus is fitted together, exhausted, and the cork brushed over with the gum several times till a satisfactory joint is obtained. In this way as good a vacuum is possible as with rubber. Working with an ordinary Bunsen pump there is no difficulty in getting 12 to 20 m.m. pressure, according to the water temperature.

Big holes, which sometimes occur, especially in large corks, are best stopped with shellac or gum slightly softened in water.

The gum is not affected by the terpenes, but hardening as the distillation proceeds, forms a perfectly air-tight covering to the cork.

In cases where the joint is frequently broken, as in repeated re-fractionation, the gum remains somewhat soft and flexible, and by simply brushing it afresh the joint is very rapidly made.

It is, of course, with the large corks that this method is of the most use and value. I have used it with corks up to 1½ inches diameter.

The same plan answers equally well for where the delivery-tube of the flask goes into the condenser, and for the cork holding the thermometer. If the neck of the distilling flask is perfectly straight and not turned over, the corks have a tendency to slip in, but this is readily avoided by cutting down a cork, rather too large, so as to form a ridge which rests on the edge of the neck.

To workers in essential oils this is invaluable; the obvious advantages being:—

1. The corks and gum are not affected by the oils, nor are the oils affected by them.
2. The corks are not spoilt, and can be used repeatedly. I have had one in use for over three months.
3. The joint is quickly made and is perfect.
4. Last, but not least, the difference in cost is very considerable, especially with large sizes.

Research Laboratories, London Essence Co.

TO CORRESPONDENTS.

J. A. Wood.—Any good makers of chemical apparatus will supply you with the distilling plant you require. A book has been written by Mr. F. Nutt on "Receipts for Home-made Wines, Cordials, &c." We do not know the publisher's name.

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THE CHEMICAL NEWS

VOL. LXXXVI., No. 2236.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION. BELFAST, 1902.

By EDWARD DIVERS, M.D., D.Sc., F.R.S., V.P.C.S.,
Emeritus Professor of Chemistry in the Imperial University of Tokyo,
Japan.

President of the Section.

(Concluded from p. 161).

WITH the laudable object of combating the prevalent notion that matter is something which is the basis or essence of a body, something acting as the medium of the manifestation of its forms of energy, a distinguished and most lucid writer on chemistry has, adequately perhaps for that object, represented a body as a compound of the various forms of energy subsisting together and cohering in certain proportions within the volume of the body. But this presentation of a subject as a cohesion or association of forms of energy is on the same footing as the presentation of ethane as consisting of two methyls bonded together, or two portions of carbon with six of hydrogen. It is compounding what cannot be had apart, what cannot be even conceived of as separate, so far as bodies are concerned. The analysis of bodies into manifestations of different properties are only mental operations. A moving body, a hot body, a green body, an explosive body, becomes by legitimate abstraction a phenomenon of motion, of heat, of colour, or of light, or a chemical phenomenon as our needs require; but the body is there all the while, and its undivided and continuous existence is indispensable to the phenomenon. The body can be hotter or colder, but not that only,—not that without other differences; red-hot iron is throughout a very different thing from cold iron, and ice differs widely from steam in most of its properties. A substance is no more composed of its properties or energies than it is composed of its so-called elements. It manifests its presence in a thousand and one ways more or less distinguishable; its properties are so to manifest itself. But no divisibility of itself while it remains itself can be thought of, no differentiation can be suggested, no nucleus with its superinduced properties can be traced.

It ought, therefore, to be possible to express all the particulars of chemical constitution without making any assumption as to substances having parts or structure. Of chemical constitution itself, I doubt whether there is to be found a definition which is not couched in language having reference to the minute mechanical structure of substances, notwithstanding the fact that all knowledge of their chemical constitution has come to us through observation of the properties of the substances themselves, and more particularly their relations in cases of double decomposition. Bearing in mind that all terms are relative, I think the chemical constitution of a substance may be defined as the resemblances shown by it in its chemical changes to other substances, often better known than it and taken as types, these resemblances being indicated and described usually by means of special nomenclature and notation. As this nomenclature and notation have been developed out of those designed to express chemical composition, it is well to point out that the notion of chemical constitution is independent of that of the latter, though clothed to some extent in its language and symbols.

The notions of radical and atom are so intimately related as to be often used indifferently, the one for the

other. The radical, ethylene, is always an atom of ethylene, the radical nitrogen always an atom of nitrogen. Radical and atom are in fact the qualitative and quantitative aspects of the same thing. They are thus exactly parallel with substance and molecule. We can think of unquantified substance, and perhaps of unquantified radical, but in chemistry we never really want such conceptions; one of the many definitions of science is the quantification of phenomena, and in every chemical phenomenon the substances concerned are quantified as molecules. The quantification of radicals expressed by the atom is fundamentally the same in principle as that of substances, namely, that of chemical equality in interaction; but it may be better to say that it is dependent upon the quantification of substances as molecules.

In the interaction of double decomposition each substance by contact and union with the other develops and manifests a dual character by becoming distributed as the two new substances, with the consequence that each of these has certain properties the same as those of the one, and certain others the same as those of the second interacting substance. What is common in this way to one of the interacting and one of the resulting substances is a radical of these substances, of which there are evidently four in every double decomposition. These radicals of a single interaction are defined as whatever two parts of the powers of a substance to yield the simple substances of its chemical composition are, in certain interactions, continued separately from each other in the two new substances. But the pair of radicals developed in the various double decompositions of a substance being by no means always the same, one of the radicals of one pair must include in its composition part or all of one of those of another pair. Acetic acid has for one pair of radicals methyl and carboxyl, and for another pair acetyl and hydroxyl. Of these, carboxyl includes hydroxyl, and acetyl includes methyl. Again, acetic acid yields the hydrogen and acetate radicals in one interaction, and hydroxyl and acetyl in another, so that in these cases the acetate radical includes acetyl and the hydroxyl includes the radical hydrogen. Now, what is common to carboxyl and acetyl and what is common to the acetate radical and hydroxyl are also treated as radicals, the one being known as carbonyl and the other as the radical oxygen. These are examples of what may be distinguished from the others as the polyvalent radicals. They are radicals of radicals, and therefore also radicals of substances. They may be defined as the common part of two or more other radicals. A single definition of all radicals can be given, but it is not instructive. A radical is any single power or any interdependent association of the powers of a substance to produce simple substances which continue in any product or series of successive products of its chemical change.

Before I leave the subject of the radical I wish to repeat that it is only when it is interacting that a substance shows a dual character or division, as it were, into parts or radicals, and that the duality it then shows is determined as much by the nature of the other substance as by its own. A substance is neither actually or conceptually the sum of its radicals. The very fact of the difference of these in different interactions should be proof of this; though it only leads to its being taken to be at least the sum of its ultimate or simple radicals. If, however, it is not the sum of its proximate radicals, it is hard to see how it can be imagined to be that of the ultimate ones. In relation to its radicals, a substance must be held to present itself as any one of these for the purpose of investigation, and at the standpoint from which it is considered. It is then to the mind that particular radical, though also something else; just as snow is white and cold, yet also something else, for the moment unconsidered. Nor can the two products of an interaction be looked upon as themselves the sum in properties of the interacting substances. To a limited extent and imperfectly, we can attach to a given radical certain of the properties common

to its compounds; but it needs no greater insight than we have already, to recognise that a substance cannot be what it is in one way, without being in that way greatly affected by what it is in another. This is now a recognised but not sufficiently considered point, and I therefore welcome those publications of Professor Vorlaender, of Halle (who now honours this Section with his presence), in which he has been vigorously calling attention to the extent to which the properties of a substance, acid, basic, stable, and what not, depend as much as, if not more, upon the interrelations of the radicals than upon the radicals themselves.

One other thing I have to say about the radical, which is as to the spelling of the word. I plead for a return to the ending of the word radical with "al," now interdicted in the *Journal of the Chemical Society*. It seems appropriate to call the powers of a substance to behave chemically as it does, the roots or radical parts of its chemical nature, but it does not seem appropriate to call them radicles or rootlets. Americans and all other nationalities but our own use the original spelling.

I have put off too long, perhaps, all reference to the properties of very dilute aqueous solutions of salts, but I wished first to discuss the nature of the radical. The osmotic pressure and other dependent points which are particular in the behaviour of such solutions are in full accordance with the assumption that an electrolyte by dissolution in much water becomes a pair or a binary system of two interdiffused quasi-substances called "ions." These ions must differ from isolated substances in bearing equal and opposite quantities of electricity; in being each unknown apart from its fellow; and in having a composition not to be found in actual substances, though identical possibly with that which a radical would have were it a substance. The ions can be indeed separated from each other, but not to continue as themselves, since in the act of separating they form ordinary substances, either by uniting with other ions, or by two molecules of ion becoming one molecule of substance. In the former way of separation the ions of two salts interact on mixing their solutions; in the other way, the ions become substances when their solution is placed in a galvanic circuit. In this mode of separation—by electrolysis, that is—the substances corresponding with the two ions, or else secondary products of their change, are produced, the one substance at the cathode and the other at the anode, while the solution away from the electrodes, but between them, remains for the time unaltered in composition. Along with this there occurs in many cases a phenomenon first recorded by Daniell, and afterwards investigated by Hittorf with such beautiful results. This consists in a greater fall taking place in the concentration of the salt solution close to one electrode than in the concentration of that close to the other, as though the ions were hydrate compounds, and that the one ion was a higher hydrate than the other. Until we know more of the nature of the ions themselves this phenomenon is most conveniently quantified on the hypothesis that the ions travel as molecular particles, but the discussion of this hypothesis is beside by present purpose.

The phenomena of ionisation or, in other words, the particular properties of dilute solutions of salts, belong evidently to a change unlike all other chemical changes. It is a polarised chemical change, in which the equivalent and complementary products of the interaction appear apart and at remote surfaces of the mass of decomposing salt solution. Two points which call for notice in connection with my present subject are that an ion is one of a pair of quantities commensurate with the quantity of the salt itself that is or would be in interaction; and that it is molecular in character and therefore to be regarded as a relative and wholly variable quantity.

Dalton's atoms were both the atoms and the molecules of present-day chemistry, but much more the latter than the former. Although the chemical atom can now be no more than a dependency of the molecule, it is commonly

set up as the starting-point in chemical theory, and as having an independent existence as a quantity of the substance, while the molecule is represented as being a conjugation of atoms. But there cannot be two standards in reference to the same thing, and in molecular chemistry the atom must give way. As I have already had occasion to point out, the atom is of the radical, the molecule is of the substance.

The four radicals of a double decomposition are equal and chemically complementary. These chemically equal quantities of such radicals are atoms. The quantities of all other radicals are also atoms, but only those of proximate radicals, those of a single interaction, are equal. Similarly, the quantities of the four substances of a single interaction are all equal and are molecules, but the quantities of substances are not equal in other interactions. These others are treated as the simultaneous occurrence of two or more single interactions, which they can always be represented and sometimes demonstrated to be. Calcium hydroxide and hydrogen sulphide give calcium hydrosulphide and water by two single interactions together, which in this case can be easily distinguished, since the calcium hydroxide will also interact with only half as much hydrogen sulphide to form the insoluble crystalline calcium hydroxyhydrosulphide and half as much water as before; this calcium salt will then interact with as much more hydrogen sulphide as went to form it, and produce the very soluble crystalline calcium hydrosulphide. Or the calcium hydrosulphide and as much calcium hydroxide as yielded it will readily interact to form twice as much as the first-obtained quantity of calcium hydroxyhydrosulphide. Thirdly, the calcium hydrosulphide and half as much water as was formed with it from calcium hydroxide readily interact to produce calcium hydroxyhydrosulphide, and half as much hydrogen sulphide as was needed to form the hydrosulphide. Therefore, and on other grounds, we say and know that one molecule of calcium hydroxide and two molecules of hydrogen sulphide give one molecule of calcium hydrosulphide and two molecules of water. This is, of course, only the law of multiple proportions introduced into chemical interactions. The expression "two or more molecules of a substance" has a meaning only as indicating the number of simultaneous or successive single interactions which have led to the conversion of certain substances into others.

Now a similar but complementary state of things meets us in the case of radicals. Instead of the coefficients of molecules, necessitated by having to consider many chemical changes as being cases of two or more single interactions occurring together, there are the valency coefficients of the polyvalent radicals, called out also by such a compound interaction. Thus, in the above case, whilst the single interaction between hydrogen sulphide and calcium hydroxide shows calciumhydroxyl as one of the radicals, the succeeding interaction between the calcium hydroxyhydrosulphide and more hydrogen sulphide shows the radical calciumhydrosulphuryl, and the common part of these two radicals is the bivalent radical, calcium. It will be evident that to give the atom of the calcium radical as bivalent is a statement reciprocal or complementary to that of giving two molecules of hydrogen sulphide as interacting with one of calcium hydroxide. Chemical equality remains still the measure of the atom, but that, in complex changes, whereas the number of molecules of one substance marks the number of single interactions, the valency number of the atom marks the same thing for the radical. It is a matter of valency, and not otherwise a matter of the atom. The radical calcium is never actively bivalent in a single interaction; in other words, it is never equal to two atoms of hydrogen. As a simple radical it does not take part in such an interaction; but it does so as a radical of radicals, such as calciumhydroxyl and calciumhydrosulphuryl, and then has the same measure as—is equal in exchange to—the atom of hydrogen, though carrying with it of necessity other

radicals, a thing the hydrogen radical never does or can do. To take another example: when acetamide is formed from acetic acid, the nitrogen of the amidogen and the oxygen of the hydroxyl are equal in exchange, but because of their valencies the one carries with it two atoms and the other one atom of hydrogen. This is no matter of merely academic contention, for upon its recognition rests the doctrine of valency itself.

The quantity of the radical is the only proper and sufficient definition of the atom, whether the radical be that of a single interaction, or a radical of radicals, that is, a polyvalent radical. The atom is, therefore, the quantified power of a substance, as the compound of the radical, to produce other compounds of the radical, including its compound with itself, where that is possible. As with the molecule of a substance, so with the atom of the radical, it is of no fixed magnitude, and may weigh a kilogram, just as well as only a milligram, or something much less. Being a relative quantity and nothing by itself, of its indivisibility there is nothing to be said outside its definition; whilst, as to its being the smallest relative quantity interchanging in an interaction, it had only thus to be defined when there was uncertainty as to the molecule and the single interaction.

It has been impossible for me to discuss the nature of the radical and the atom without referring to valency, but it is itself a subject of such importance as to need special consideration. It does not seem right to me to say even the little I can say about valency without naming with the respect they deserve from us the distinguished chemists who laid the foundations of the doctrine and developed it:—Williamson, Odling, Wurtz, Edward Frankland, and Kékulé. I had the good fortune to be in the same laboratory as, and then intimate with, Kékulé, when in 1854 he was working out the bivalency of sulphur and oxygen by his investigation of thioacetic acid, some time, that is, before he had thought out the benzene ring and the valency of carbon.

Only when, as is usual, propositions are made in which a separate and independent existence, with valency as a property, is imputed to a radical, does the question, as to what valency is, present any difficulty. Approaching it from the side of the molecule and of double decomposition, and therefore from the experimental side instead of from that of the radical itself, as is customary, valency presents itself as being the number of single interactions necessary, in order to have a certain radical occur, first as that of one substance, and then as that of another which has no other radical in common with the first substance. That ammonia possesses one atom of the radical nitrogen, and three atoms of the radical hydrogen, and that the nitrogen radical is trivalent and the hydrogen radical univalent are statements mutually based upon facts such as the following:—Potassium nitrosulphate, which contains nitrogen but no hydrogen, is converted by water in a sharply defined single interaction, into potassium-hydrogen sulphate, and into potassium imidosulphate, a substance which contains all the nitrogen along now with hydrogen. This salt passes, also sharply and by a single interaction with water, into as much more sulphate along now with potassium amidosulphate, which latter substance contains all the nitrogen and twice as much hydrogen as belonged to the imidosulphate. Lastly, the amidosulphate interacting with water gives a third quantity of potassium sulphate, equal to the last, and also ammonia, having all the nitrogen of the nitrosulphate started with, three times as much hydrogen as the imidosulphate, and nothing else. That is to say, the nitrosulphate and the ammonia have no other radical than the nitrogen the same, while three single interactions have been necessary to separate in this way the nitrogen radical from the three atoms of the potassium-sulphonyl radical. Therefore the nitrogen radical is trivalent and its quantity is the atom. Again, there are three atoms of the univalent hydrogen radical in the ammonia molecule, because in each of the three interactions an equal quantity of this radical is brought in from water.

Ammonia shows only one pair of radicals, behaving, so far as its own interactions go, exclusively as a compound of amidogen and hydrogen, and these radicals are referred to as united or bound together in being ammonia. It is only the interactions of its derivatives, primary, secondary, and tertiary, that are indicated by treating the amidogen as ultimately nitrogen and two hydrogen radicals. But this involves the consideration of all three hydrogens as bound to the nitrogen; and it becomes, therefore, of vital importance to bear in mind that the hydrogen radical, proper to the ammonia itself, is bound to a nitrogen radical which carries also bound to it two other hydrogen radicals.

Chemical formulæ still remain to be considered. They are symbolisations of deductions from experimentally ascertained facts, and are independent of the interpretation commonly given to them as referring to the minute differentiated structure of substances. A chemical equation expresses a chemical change quantitatively by means of chemical formulæ which are molecular. In a case of double decomposition, therefore, there are four formulæ; but when two or more such interactions are expressed in one equation, because they occur together, the formulæ of transition-substances do not appear, and then numerals before formulæ tell the number of interactions in which separate molecules of the substance have taken part. A formula represents the relative interacting quantity or molecule of a substance, while the single symbols composing it stand each for an atom of the radical of a certain simple substance as possessed by the substance formulated. The connecting lines and dots, and certain collocations of the symbols, indicate the association of the simple radicals as compound radicals in different interactions.

What is symbolised by position formulæ, and indeed by the formula altogether, are the chemical activities and abilities of the substance and its derivatives, and their analogies with those of other substances. When not in interaction, a substance has no constitution and no formula. It is certainly not on any experimental grounds that it can be regarded as some spatial arrangement of unlike parts. To take the simplest case; if we start with sodium hydroxide and symbolise its molecule by some mark, such as X to begin with, the interaction of the substance with an acid leads us to replace the X by two symbols and a connecting mark. One of these will be Na for the sodium radical; let the second be Z for the other radical, and let a dot or stroke be placed between the symbols to mark them as those of a pair of radicals in interaction. In other interactions, such as that with melted potassium acetate, we find need for a new pair of symbols, one being H for the hydrogen radical, while the other may be Q. But it is easy to decompose two molecules of sodium hydroxide in one operation into molecules of sodium, hydrogen, and oxygen, from which fact we learn that Z is replaceable by the double symbol O—H, and Q by O—Na. Thus, Na—Z and H—Q become equally Na—O—H, which records the ultimate radicals of sodium hydroxide, together with all its interactions, immediate and remote. But it does this with no more implication of spatially placed and tied parts than is made by expressing the measured flow of time by a straight line, or than is to be found in t^2 seconds of time, or in c^3 as the third power of a number, unless we specifically condition this symbol as stereometric. A formula is not to be read—on experimental grounds, I mean—as a symbol of parts juxtaposed and joined on, and should be regarded as an intricate but legible monogram telling the chemical nature of the substance. Every symbol in it is to call to mind a phase of the chemical activity of the substance or of its derivatives, a phase that may be for the time as the substance itself to the investigator, just as a pigment substance becomes only a red or a white to the painter. For example, salt is often nothing more than its chlorine phase to the chemist when he wants only a soluble chloride; whether it is of potassium, sodium, or ammonium, then matters not to him.

The double linking of the carbons in ethylene is a symbolised expression of facts, without reference to hypothesis. The two carbon radicals of ethane or of alcohol behave together just as does the single carbon of methane or the nitrogen of ammonia in being, but with a valency of six, continued to other compounds devoid of all the other radicals of the ethane or alcohol—that is, of the hydroxyl and the hydrogens. The quadrivalency of each carbon is made up by the interaction necessary to dissociate or to bring together the two methyls, which counts as a unit of valency to each carbon. Ethyl hydrogen sulphate decomposes into sulphuric acid and ethylene, the hydrogen-sulphate radical with a hydrogen radical becomes the acid as the one product, while the methylene radicals again pair off as the two methyls had done when ethane was formed, thus producing the non-saturated substance, ethylene. Since there is a perchlorethylene, the second linking mark falls between the two carbons; and when ethylene passes back to an ethane compound two units of valency are displayed by it without the carbons becoming dissociated.

Position formulæ of isomerides, such as those of propyl alcohol and acetone, present no difficulty, because they are interpreted as the expressions of unlike double decompositions. It is not unfrequently the case that no constitutional or structural formula can be given to a substance which shall express all the pairs of radicals possible in its interactions, of which the best studied example is that of ethyl acetoacetate. This state of things, known as tautomerism, admits of no other interpretation than that there are really two substances existent, of which one only is known, the other or so-called "pseudoform" requiring the assumption of its existence as a transition substance only. The notion of the shifting hydrogen radical is but the hypothetical way of viewing the intervention of the intramolecular change by which the substance becomes its "pseudoform."

The cyclic formula of benzene expresses the fact that, unlike a fatty hydrocarbon, benzene shows but one pair of interaction radicals, hydrogen and phenyl. The "ortho-," "meta-," and "para" positions in benzene derivatives are only expressions of facts of "position" isomerism, such as those pertaining to other non-saturated compounds, but more complex to unravel and more varied and interesting. It is doubtful whether the Kékulé ring does not remain as efficient a symbol as any stereographic substitute yet proposed for it; but it itself is purely a symbol of chemical interactions, and has no spatial significance other than what may be put into it by convention. "Adjacent," "opposite," and the like have only application literally to the arrangement of the symbols; but if the symbolisation is perfect the "opposite" carbons will, as a matter of course, always indicate the same point concerning the chemical interactions.

Whether the chemical formulæ for the lactic acids are better arranged in a plane or as a tetrahedron is to be decided by the facts concerning these and other asymmetric carbon compounds, the object being to symbolise or formulate as distinct and complementary in certain physical properties, but alike in their chemical interactions, two isomeric substances, simultaneously formed in molecular quantities. Enantiomorphous arrangements of the respective formulæ of dextro- and lævo-lactic acids fully meet the case, but the facts are in no way explained by these formulæ. In the enantiomorphously related hemihedral crystals of the corresponding salts of the dextro- and lævo-acids, and in their opposite rotatory effect in solution upon the plane of polarised light, we recognise something like a torsioned state of the whole homogeneous substance, something to be accounted for by peculiarity of chemical origin, but not something made more intelligible by any imagined arrangement of unlike parts. It is possible to give an account of the chemical facts without making reference to mechanical structure, and then to reason about them somewhat in the following way:—Given the case of a

substance doubly equipped with the power to take part in a certain interaction, and considering that the exercise of the power can only be single, and that it cannot be made without affecting and transforming, or perhaps nullifying, the second equipment with power, predict what will happen. This is the prediction called for concerning any interaction which generates an asymmetric carbon compound. The result could never have been predicted; yet how natural and beautiful it is when it comes to us through experiment enlightened by the genius of Pasteur, Le Bel, and van't Hoff! That answer is that a twinned substance results, one indeed in most respects and chemically, but two in certain physical properties, characterised by presenting phenomena as of equal and opposite strains, a polarised pair of substances, in fact. What I mean by the double equipment with power is, of course, the pair of identically related and self-identical radicals, or the bivalency of one radical wholly and directly associated with the carbon radical. The case of the oxygen radical of aldehyde is that of the bivalent radical; the other case is that of the two carboxyl radicals of hydroxy-tartronic acid, or that of the two methylene hydrogen radicals of alcohol which these carboxyls have replaced. The tetrahedral formula with its reflected form admirably symbolises the case of enantiomorphously related pairs of substances. But no light whatever is thrown upon the nature of this pairing by the tetrahedron model; its value depends upon the fact that as a symbol it so fully matches the constitution of the substances.

Here I bring my summary of chemical theory and its formulation without hypothesis to a conclusion, hoping that, to some extent, I may have impressed you with the fact that the exposition of even advanced chemistry, in its symbolic, equally as in its ordinary language and nomenclature, is independent of any hypothesis as to the mechanically and chemically differentiated structure of substances, and that chemistry can be studied and still further developed without reference to such a structure. I have asked for few or no reforms in the use of either terms or symbols, my point having been only to press for a consideration and discussion of the doctrines of chemistry and the great atomic theory itself as something concerned exclusively with experimental chemical facts.

THE SYNTHETICAL ACTION OF ENZYMES.*

By Dr. E. FRANKLAND ARMSTRONG.

It has long been known that enzymes have the power of inducing hydrolysis, particularly of disaccharides containing a "glucoside-linkage," but the observation of Croft Hill that enzymes can also effect synthetical changes is of quite recent date; his experiments have shown that when maltose is hydrolysed by maltase, just as in the case of the hydrolysis of esters by acids, a reversible action takes place in concentrated solutions; and that in concentrated solutions of glucose a disaccharide is formed. Some uncertainty exists as to the nature of this sugar, Hill claiming that it is maltose, whereas Emmerling contends that he has identified it by means of the phenylosazone with isomaltose. Bearing in mind the great difficulty experienced in purifying and characterising the osazones of disaccharides, it is impossible, on the strength of this one derivative alone, to decide the question; but as Emmerling has shown that the sugar formed is not fermented by "top yeast," it may be concluded that it cannot be maltose.

Croft Hill's conclusion that enzymes exercise synthetic functions has been justified by the later observations of Kastle and Loevenhart and of Hanriot on lipase, the

* Read before the British Association (Section E), Belfast Meeting, 1902.

enzyme by which fats are hydrolysed, these observers having shown that this enzyme is capable of producing both esters of fatty acids and glycerides. In these cases stereochemical isomerism is out of the question, and the products are identical with the natural substances. Emmerling has also demonstrated that the synthesis of amygdalin from mandelio-nitrile glucoside and glucose may be effected by means of maltase.

It is interesting to note that Fischer has proved that isomaltose, not maltose, is formed by the action of acids on glucose, showing that in their case the action is not strictly analogous to the reversible hydrolysis of esters by acids, and it is, therefore, the more probable that isomaltose should be formed by the action of enzymes, as their behaviour in other respects resembles that of acids. Unfortunately nothing is known as to the relationship of isomaltose to maltose, and it is impossible to say whether they are merely the α - and β -glucoside forms, or whether they differ as regards the carbon atom to which the glucoside linkage is attached.

The author has been engaged in studying lactase in conjunction with Professor E. Fisher, and they have been able to demonstrate that this enzyme is one of those which are capable of inducing synthetical changes.

It was found that, whereas the action of lactase on milk-sugar was at first hindered and ultimately stopped entirely by the presence of the monosaccharides to which it gives rise; when the amount of these was further increased a change in the reverse direction took place. Accordingly the enzyme was kept for some time at 35° in a concentrated solution containing equal parts of galactose and glucose, toluene being added as an antiseptic. Both the reducing power and the optical rotatory power of the solution diminished steadily, and the phenylhydrazine test showed that a sugar was present capable of forming an osazone which was easily soluble in hot water. The tests, in fact, united in proving that a disaccharide had been produced. After three weeks, the rotatory power of a 50 per cent solution had fallen to about 16–20 per cent, indicating that roughly 20–25 per cent of the glucose had been converted into disaccharide; this conclusion was confirmed by the change in the reducing power. The isolation of the sugar in a pure state has not yet been effected.

The properties of its phenyllosazone resemble those of phenyllactosazone. More light has been thrown on the nature of the sugar by the study of its behaviour towards other enzymes. Having proved that the sugar—which has been termed provisionally *Isolactose*—is unfermentable by "top yeast," the solution, obtained in the manner described, was boiled, diluted, and subjected to fermentation in order to remove the major portion of the unchanged monosaccharides; it was then concentrated, and its behaviour studied towards "bottom" yeast, emulsin, and kefir lactase. All the usual precautions were observed, the extent to which changes took place in the solution was ascertained by determining its reducing power and its rotatory power, when possible, and especially by means of the phenylhydrazine test.

In this way it was proved that, whilst isolactose is entirely fermented by "bottom yeast," and hydrolysed by lactase, emulsin is without any action upon it. Tabulating the behaviour of the natural and synthetic sugars, it is obvious that the two are distinguished by their behaviour towards bottom yeast and emulsin; their relationship is, therefore, of the same order as that which obtains between the α - and β -alkyl-glucosides.

Milk-sugar:—	Top yeast		Unchanged
	Bottom yeast		Unchanged
	Emulsin		Hydrolysed
	Lactase		Hydrolysed
Isolactose:—	Top yeast		Unchanged
	Bottom yeast		Fermented
	Emulsin		Unchanged
	Lactase		Hydrolysed

It is, at any rate, certain that milk-sugar is not formed, so that in the case of lactase, as in that of maltase, a sugar isomeric with that normally hydrolysed by the enzyme is obtained as the product of its synthetic activity.

Lactase also exercises a reversible action, though to a much less extent, in a concentrated solution of glucose. In this case, also, a disaccharide is formed which is characterised by yielding a very soluble phenyllosazone. On the other hand, little or no synthetical action is effected by lactase in a solution of galactose.

Finally, experiments carried out in an exactly similar manner with *emulsin* show that this enzyme is also capable of effecting synthetical changes, and that it acts in a particularly rapid manner. The maximum of reversion is effected in a concentrated (50 per cent) solution containing equal parts of glucose and galactose, an equilibrium being arrived at when about 20 per cent of disaccharide is present. Reversion also takes place in a concentrated solution of glucose under the influence of *emulsin*. The products afford phenyllosazones which are easily soluble in hot water, and are not fermented by top yeast, but easily by bottom yeast.

It may, therefore, be regarded as established that the enzymes which induce the hydrolysis of glucosides are also capable of acting reversibly in concentrated solutions of the glucoses; the disaccharides which are thus produced, however, are isomeric, not identical with those normally hydrolysed by the enzymes, and in this respect, therefore, the condensing action of enzymes is comparable with that of concentrated solutions of mineral acids.

RECENT SYNTHETICAL RESEARCHES IN THE GLUCOSIDE GROUP.*

By Dr. E. FRANKLAND ARMSTRONG.

If anhydrous hydrogen chloride or bromide be allowed to act at ordinary temperatures on either of the two isomeric pentacetyl-derivatives of glucose, the acetyl radicle attached to the aldehyde group is quantitatively displaced by halogen, giving rise to isomeric aceto-halogen-glucoses, which are well-defined crystalline substances. These compounds are of considerable value as synthetical agents. One of them was made use of by Michael some twenty years ago, in the form of a syrup, in effecting the synthesis of helicin and some other glucosides derived from the phenols. In practice the interaction between the halohydrate and the acetyl-derivative is carried out in sealed tubes, the gases being liquefied by the aid of liquid air. When the interaction is at an end, the tubes are again immersed in liquid air in order to allow of their being opened safely. The aceto-halogen-glucoses are completely converted into the alkylglucosides by treatment with alcohols, giving rise, when methyl alcohol is used, to the known α - and β -methylglucosides.

As the glucosides are obtained in a pure state by this method they crystallise without much difficulty. The β -derivatives are specially easy to obtain, whereas when Fischer's method is used, which involves heating a mixture of the sugar and alcohol together with a small quantity of chlorhydric acid, the greater part of the product is the α -glucoside; the methods therefore supplement one another. A series of alkyl derivatives of glucose and of galactose have been investigated.

Aceto-halogen-derivatives of both maltose and milk-sugar have been prepared, and the former converted into the corresponding β methylmaltoside—the simplest case of a trisaccharide. The behaviour of this compound towards enzymes is specially interesting. As Fischer has shown, maltose is an α -glucoside,† but in the synthetic

* Read before the British Association (Section B), Belfast Meeting, 1902.

† α -Glucosides are those hydrolysed by maltase, β -glucosides those hydrolysed by emulsin.

compound the methoxy-group is introduced into the β -position. Methylmaltoside is, in fact, a double $\alpha\beta$ -glucoside similar to the natural glucoside amygdalin, and resembles this latter in its behaviour with yeast maltase, the maltose part of the molecule being hydrolysed, so that methylglucoside and glucose are formed; on the other hand, when subjected to the action of emulsin, the maltoside is resolved into methyl alcohol and maltose. An exactly analogous behaviour is shown by the corresponding phenolmaltoside.

Recently, β -acetochloro-derivatives of sugars have been prepared by Skraup by the action of phosphorus pentachloride and aluminium chloride on the pentacetyl-derivatives; but in this case molecular rearrangement takes place, both the α - and β -pentacetates giving the same chloro-derivatives. The investigation carried out by the author has shown that the β -halogen-derivatives are the more stable, and that in the presence of alkali the α - are rapidly converted into the β -derivatives, which is a definite proof that the isomerism and likewise that of the glucosides is stereochemical. This instability has unfortunately prevented a synthesis of the α -glucosides of the phenols; and it is of interest to note that nearly all the natural glucosides, which have been tested physiologically, belong to the β -series.

Glucosides of the type of milk-sugar and maltose have been prepared by the interaction of the aceto-halogen-glucoses and the sodium derivatives of the glucoses, and have been isolated in the form of phenylosazones; these osazones are soluble in boiling water and they are converted by the action of benzaldehyde into keto-aldehydes or *osones*, which resemble glucosone in their properties. The disaccharide obtained from acetochlorogalactose and sodium glucose very closely resembles, if it is not identical with, melibiose—the phenylosazones and bromphenylosazones prepared from the natural and synthetic products being indistinguishable, as well as the behaviour of the two sugars towards enzymes. It is noteworthy that the osones derived from the disaccharides resemble the parent sugars in their behaviour towards enzymes and that they, too, exercise a highly selective action.

THE ACTION OF DISTILLED WATER UPON LEAD.*

By Professor FRANK CLOWES, D.Sc.

WHEN lead is placed in contact with ordinary distilled water, chemical action becomes evident by the formation of a *white deposit* which contains lead, and lead is also found in *solution* by chemical tests.

The lead appears to exist *in solution* in the form of hydroxide, since it is removed by passing the liquid through filter-paper; this fixation by cellulose of the dissolved hydroxide is one of the marked properties of the hydroxide. The hydroxide is readily removed from the cellulose by dilute acetic acid.

An examination of the *white deposit* proved that it was a hydroxycarbonate, containing three molecules of carbonate to one of hydroxide.

It would be inferred from the above facts that the lead is probably converted into hydroxide by the action of the oxygen dissolved in the water, and that the subsequent action of the dissolved carbon dioxide converts the hydroxide into hydroxycarbonate.

It would appear improbable that even bright lead can decompose water with formation of hydroxide. But the opinion has prevailed that the action of distilled water on lead is promoted by the presence of carbonic acid.

The nature of the action of distilled water upon lead was studied by exposing bright lead, both *in vacuo* and in

an atmosphere of hydrogen, to distilled water which had been freed from its dissolved gas by boiling; and then introducing either oxygen alone, carbon dioxide alone, or mixtures in varying proportions of oxygen with carbon dioxide.

Bright sheet lead of great purity, when exposed to boiled distilled water *in vacuo* or in an atmosphere of hydrogen, was acted upon only to an infinitesimal extent (0.3 part of lead to one million parts of water). This result was probably due to the impossibility of removing the last traces of oxygen, and it negatives the suggestion of any direct action of water upon lead.

When the lead was exposed to the water in the presence of the different artificial atmospheres, the action reached its greatest extent (0.023 part of lead per 100 of water) when oxygen alone was present; with carbon dioxide the action was slight (0.008 per cent); with equal volumes of oxygen and carbon dioxide about an equal effect was produced; while with eight volumes of oxygen to one of carbon dioxide the extent of the action approached that due to oxygen.

It is evident, therefore, that dissolved oxygen is the cause of the action of distilled water upon lead, the subsequent action of carbonic acid leading to production of hydroxycarbonate. It is further evident that the presence of carbon dioxide in any large proportion exerts an inhibitory effect upon the action.

When sheet lead is immersed in ordinary distilled water with exposure to air, it is found that the rate of action is diminished by total immersion as compared with partial immersion, but that in both cases the total result produced is ultimately the same.

In the earlier stage of the above inquiry the ordinary aerated distilled water was freed from its dissolved gases by being boiled in glass vessels. When this water was allowed to re-aerate itself by exposure to the air, it did not regain its original power of acting upon lead. This was found to be due to the inhibitive power of silicates dissolved from the glass, and the inhibitory power varied with the degree of solubility of the glass, when vessels composed of different kinds of glass were used. Boiling the water in glass, or condensing the steam in glass tube-condensers, lead to the inhibitory effect; but contact of cold distilled water with cold glass did not produce the result. Complications arising from this cause were avoided in later experiments by distilling the water from a copper vessel and condensing the steam in a copper tube-condenser.

It has been suggested that the action of water on lead is indirectly due to the presence of bacteria. In the above experiments, water sterilised by long boiling was frequently exposed to lead which had been fused in a flask sterilised by steam in the presence of air which had passed through cotton-wool; the oxidising action occurred freely in all such experiments, presumably in the absence of bacteria and their products.

The action of distilled water, or of soft waters generally, upon lead may be considerably reduced by dissolving various substances in the water. Sulphuric acid, or a sulphate, was found to be most efficient for this purpose; carbonic acid and carbonates proved less efficient; lime-water was still less effective, and even promoted the action when it was used in larger proportion.

Business Illustrated: an Unconventional Magazine-review. Vol. I., No. 1, July, 1902.—The especial function which *Business Illustrated* has set itself to fulfil is the useful but unconventional one of supplying business people with a publication which stands midway between the trade and technical journals on the one hand and the popular magazine on the other. The new periodical is well and chattily written, and printed on thick glazed paper, while the illustrations are all that can be desired. We wish our young contemporary every success.

* Read before the British Association (Section B), Belfast Meeting, 1902.

THE
RADIO-ACTIVITY OF THORIUM COMPOUNDS.*

II. THE CAUSE AND NATURE OF RADIO-ACTIVITY.

By E. RUTHERFORD, M.A., D.Sc.,
Macdonald Professor of Physics, McGill University, Montreal,
and
FREDERICK SODDY, B.A. (Oxon.),
Demonstrator in Chemistry, McGill University, Montreal.

(Concluded from p. 135).

10. *The Nature of the Radiations from Thorium and ThX.*

It has recently been found (Rutherford and Grier, *Phys. Zeit.*, 1902) that thorium compounds, in addition to a type of easily absorbed Röntgen rays non-deviable in the magnetic field, emit also rays of a very penetrating character deviable in the magnetic field. The latter are therefore similar to cathode rays, which are known to consist of material particles travelling with a velocity approaching that of light. But thorium, in comparison to uranium and radium, emits a much smaller proportion of deviable radiation.

From the view of radio-activity put forward, it necessarily follows that the total radio-activity of thorium is altered neither in character nor amount by chemical treatment. This conclusion can be tested by comparing the radiations of thorium and ThX with the mixture which constitutes the thorium radiation. It must, however, be pointed out that it is difficult to make any absolute measure of radio-activity, on account of the different extents in different cases to which the radiations are absorbed in the material of the substance emitting them. The total radio-activity of the original thorium is derived from a small quantity of the substance in the form of powder, while the radiations from ThX are produced by a very thin film of the material on a platinum dish. The radiation from thorium is half absorbed by a thickness of aluminium 0.0004 c.m. thick, and as thorium oxide is far denser than aluminium, it is probable that the radiation in this case is confined to a surface layer only 0.0001 c.m. deep. In the ThX, on the other hand, there is probably but little absorbed in the substance itself. The difficulty can be overcome to some extent by taking for the comparison the radio-activity of a thin film of a soluble thorium salt produced by evaporating a solution to dryness over a large metal plate. Compared in this way, the radio-activity of ThX when first separated almost exactly equals the activity of the nitrate from which it is produced, while the hydroxide retains about two-fifths of this amount. The difference is in the expected direction, for it is certain that more absorption takes place in the nitrate than in the products into which it is separated. The requirements of the hypothesis can thus be said to be satisfied, but the example illustrates the difficulty of making absolute measurements of radio activity. These throughout have almost completely been avoided. It is possible to trace with great accuracy the change of radio-activity of any preparation by leaving it undisturbed on its original plate, and comparing it always with the same comparison sample. But to express the radio-activity of one body like ThX in terms of that of another like ThX, except for the purposes of comparison, is misleading, as the above consideration shows.

Similar difficulties stand in the way of an answer to the second question—whether the nature of the radiations is affected by chemical treatment,—for it has been experimentally observed that the penetration power of these radiations decreases with the thickness of material traversed. The character of the radiations from ThX and thorium have, however, been compared by the method of penetration power. A large number of comparisons justifies the view that the character of thorium radio-activity is unaltered by chemical treatment and the separation of ThX, although the different types are unequally distributed among the separated products.

* Communicated by the Authors.

The determination of the proportion between the deviable and non-deviable rays affords a new means of approaching the question. The general result is that the radiations from ThX and the excited radiation it produces both comprise deviable and non-deviable radiation. But in the experiment in which the excited radiation was allowed to spontaneously decay—by removing the ThX as formed—the final product, after twenty-three precipitations, was found to be quite free from deviable radiation. This, as will be shown in a following paper, is one of the most striking resemblances between the non-separable radio-activities of uranium and thorium.

Finally, it may be mentioned that the proportion of deviable and non-deviable radiation is different for different compounds of thorium. The nitrate and ignited oxide, compounds which hardly possess any emanating power, have a higher proportion of deviable radiation than compounds with great emanating power. This is indirect evidence of the correctness of the view already put forward (Section 7), that when the emanation is prevented from escaping, it augments the proportion of excited radio-activity of the compound.

11. *Summary of Results.*

The foregoing experimental results may be briefly summarised. The major part of the radio-activity of thorium—ordinarily about 54 per cent—is due to a non-thorium type of matter (ThX) possessing distinct chemical properties, which is temporarily radio-active; its activity falling to half value in about four days. The constant radio-activity of thorium is maintained by the production of this material at a constant rate. Both the rate of production of the new material and the rate of decay of its activity appear to be independent of the physical and chemical condition of the system. The ThX is undergoing a further change, and one of the products is gaseous, and in the radio-active state constitutes the emanation produced by thorium compounds. The ThX further possesses the property of exciting radio-activity on surrounding inactive matter, and about 21 per cent of the total activity under ordinary circumstances is derived from this source. Its rate of decay, and other considerations, make it probable that it is the same as the excited radio-activity produced by the thorium emanation, which has been shown to be produced by ThX. There is evidence that if by any means the emanation is prevented from escaping in the radio-active state, the energy of its radiation goes to augment the proportion of excited radio-activity in the compound.

Thorium can be freed by suitable means from both ThX and the excited radio-activity which the latter produces, and then possesses an activity about 25 per cent of its original value, below which it has not been reduced. This residual radiation consists entirely of rays non-deviable by the magnetic field, whereas the other two components comprise both deviable and non-deviable radiation. Most probably this residual activity is caused by a second non-thorium type of matter produced in the same change as the ThX, and it should therefore prove possible to separate it by chemical methods.

12. *General Theoretical Considerations.*

Turning from the experimental results to their theoretical interpretation, it is necessary to first consider the generally accepted view of the nature of radio-activity. It is well established that this property is the function of the atom and not of the molecule. Uranium and thorium, to take the most definite cases, possess the property in whatever molecular condition they occur, and the former also in the elementary state. So far as the radio-activity of different compounds of different density and states of division can be compared together, the intensity of the radiation appears to depend only on the quantity of active element present. It is not at all dependent on the source from which the element is derived, or the process of purification to which it has been subjected, provided sufficient time is allowed for the equilibrium point to be

reached. It is not possible to explain the phenomena by the existence of impurities associated with the radio-active elements, even if any advantage could be derived from the assumption. For these impurities must necessarily be present always to the same extent in different specimens derived from the most widely different sources; and, moreover, they must persist, in *unaltered amount*, after the most refined processes of purification. This is contrary to the accepted meaning of the term impurity.

All the most prominent workers in this subject are agreed in considering radio-activity an atomic phenomenon. M. and Mme. Curie, the pioneers in the chemistry of the subject, have recently put forward their views (*Comptes Rendus*, 1902, cxxxiv., p. 85). They state that this idea underlies their whole work from the beginning, and created their methods of research. M. Becquerel, the original discoverer of the property for uranium, in his announcement of the recovery of the activity of the same element after the active constituent had been removed by chemical treatment, points out the significance of the fact that uranium is giving out cathode rays. These, according to the hypothesis of Sir William Crookes and Professor J. J. Thomson, are material particles of mass one-thousandth of the hydrogen atom.

The present researches had as their starting-point the facts that had come to light with regard to the emanation produced by thorium compounds and the property it possesses of exciting radio-activity on surrounding objects. In each case the radio-activity appeared as the manifestation of a *special kind of matter* in minute amount. The emanation behaved in all respects like a gas, and the excited radio-activity it produces as an invisible deposit of intensely active material, independent of the nature of the substance on which it was deposited, and capable of being removed by rubbing or the action of acids.

The position is thus arrived at, that radio-activity is at once an atomic phenomenon and the accompaniment of a chemical change in which new kinds of matter are produced. The two considerations force us to the conclusion that radio-activity is a manifestation of sub-atomic chemical change.

Before such a view was entertained, the possibility of explaining the results obtained on the existing hypotheses was fully considered. But the attempt was unsatisfactory, and involved the assumption of many new conceptions which cannot be experimentally verified, and which are, moreover, not in accordance with what is already known of radio-activity. It is apparent in radio-activity that we are dealing with phenomena outside of the sphere of known atomic forces, for the whole process proceeds independently of temperature and chemical affinity. So that even if the accepted views were altered, and the radio-active elements regarded as compounds that had not yet been resolved, it would not assist in the interpretation of the facts. Besides, there is not the least evidence for assuming that uranium and thorium are not as homogeneous as any other chemical element, in the ordinary sense of the word, so far as the action of *known* forces is concerned. The idea of the chemical atom in certain cases spontaneously breaking up, with evolution of energy, is not of itself contrary to anything that is known of the properties of atoms. For the causes that bring about the disruption are not among those that are yet under our control, whereas the universally accepted idea of the stability of the chemical atom is based solely on the knowledge we possess of the forces at our disposal.

The changes brought to knowledge by radio-activity, although undeniably material and chemical in nature, are of a different order of magnitude from any that have before been dealt with in chemistry. The course of the production of new matter which can be recognised by the electrometer by means of the property of radio-activity after the course of a few hours, or even minutes, might possibly require geological epochs to attain the quantities recognised by the balance. However, the well-defined

chemical properties of both ThX and UrX are not in accordance with the view that the actual amounts involved are of this extreme order of minuteness. On the other hand, the existence of radio-active elements at all in the earth's crust is an *a priori* argument against the magnitude of the change being anything but small.

It is a significant fact that the radio-active elements are all at the end of the periodic table. If we suppose that radium is the missing second higher homologue of barium, then the known examples—uranium, thorium, radium, polonium (bismuth), and lead—are the five elements of heaviest atomic weight. Nothing can yet be stated of the mechanism of the changes involved; but whatever view is ultimately adopted, it seems not unreasonable to hope that radio-activity affords the means of obtaining information of processes occurring within the chemical atom.

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THE REVERSION OF SUPERPHOSPHATE OF LIME IN THE SOIL.

By W. F. SUTHERST, Ph.D., A.I.C.

SUPERPHOSPHATE of lime is manufactured by the action of strong sulphuric acid on any substance containing a large amount of tricalcic phosphate, such as coprolites, bones, &c., sufficient acid being employed to combine with two-thirds of the total calcium, forming calcium sulphate and monocalcium phosphate, soluble in water. This product has been used with very great success as a manure for a number of years, and at the present time constitutes the chief source of phosphoric acid for fertilising purposes. It is usual to add this manure to the soil in quantities varying from 2 to 5 cwt. per acre, according to the kind of crop grown.

Nearly the whole of the phosphoric acid present in superphosphate is—or should be—soluble in water; when freshly made there is more soluble than on keeping, the monocalcic salt changing slowly to the dicalcic. But when applied to the soil the plants do not take it up in that form, since it has been shown that free acid (especially mineral) kills most plants very quickly, but it first undergoes a change, being rendered insoluble by several ingredients present, the chief ones being carbonates of calcium and magnesium, oxides of iron and aluminium—in fact, any oxide or carbonate of a base which happens to be present. The acid- or water-soluble phosphate, then, when it comes in contact with the soil, combines with these ingredients, forming insoluble calcium, magnesium, or iron phosphates; and it is from these compounds that the plants obtain the phosphoric acid necessary for their growth, the acid sap of their roots being capable of dissolving to some extent these compounds, and by the process of diffusion absorbs them into the plant system.

This process of precipitation or reversion does not by any means take place instantly; many days elapsing before all the water-soluble phosphate is rendered insoluble, and that only when a large excess of the reverting agents are present—a state of things not always occurring.

Should there be only small quantities of chalk or iron oxide present the superphosphate is liable to be washed out of the soil, especially if of a sandy nature; this easily explaining the reason why light sandy soils give such poor results when superphosphate or other soluble fertilisers are applied.

To observe which ingredient of the soil was most active, and also to find how much of each was necessary to revert the soluble phosphate, a series of experiments were carried out by me in the laboratories of the Agricultural College, Holmes Chapel. The experimental part was carried out in the following manner:—In a number of flasks a known weight of superphosphate of known strength was mixed with water, and to this solution various amounts of chalk,

magnesium carbonate, and limonite (the latter representing as near as possible the oxide of iron in the soil), and from these at different periods samples were taken and the phosphoric acid still soluble in water estimated by the ammonium molybdate and magnesia mixture method; most of the estimations being carried out most assiduously by Mr. F. C. Harold, one of my students. The following table gives the amount of each ingredient used to one part of superphosphate, the time taken for reversion, and the amount of phosphoric acid still in solution.

Parts super-phosphate, containing 22·7 per cent sol. P_2O_5 .	$CaCO_3$ added.	Time taken for reversion.	P_2O_5 still in solution.	Per cent in solution to per cent total P_2O_5 .
Parts.				
I	9	15	0·044	19·59
I	12	15	0·040	17·70
I	24	15	0·022	9·70
$MgCO_3$ added.				
I	9	9	0·014	6·12
I	12	9	0·0024	1·06
I	24	6	0·0019	0·83
Limonite added.				
I	9	9	0·046	20·26
I	12	9	0·038	16·74
I	24	9	0·0091	4·00

From the above results it appears that the magnesium carbonate is the most active reverting agent, the oxide of iron next, and the calcium carbonate the least of all; in each case, however, some portion of the phosphate remained in solution.

The soil generally contains more oxide of iron than any of the other ingredients, except in the case of the soils resting on chalk, so that in most cases the soluble phosphate is precipitated chiefly as an iron compound, the remainder combining with the calcium and magnesium carbonates. Now, it is from these compounds that the root-sap takes up phosphoric acid, but only the calcium and magnesium compounds are taken up (the iron phosphate not being soluble), so that by adding superphosphate to ordinary soils only about one-half is available for plant food. To prove this, mixtures were made up of calcium and magnesium carbonates and limonite, and to these were added a known amount of superphosphate, together with water. After standing some days, the amount of phosphoric acid still in solution was determined, and after this a portion of the contents was treated with 1 per cent citric acid solution (this being Dyer's method of representing the acidity of root-sap), and the phosphoric acid dissolved out estimated. The following table gives the results:—

Mixture.	Time taken for reversion. Days.	P_2O_5 in solution to total P_2O_5 . Per cent.	P_2O_5 soluble in citric acid. Per cent.
1. Representing a clay soil. Containing 10 parts limonite, 4 parts $CaCO_3$, 1 part $MgCO_3$	12	12·64	54·00
2. Representing a loamy soil. 10 parts limonite, 2 parts $CaCO_3$, 1 part $MgCO_3$	12	14·34	50·00
3. Representing a loamy soil. 10 parts limonite, 1·5 parts $CaCO_3$, 20 parts $MgCO_3$	12	14·40	49·40

The neutral or basic phosphatic manures, such as basic slag or basic superphosphate, are in the insoluble form already, and being combined chiefly with calcium, the greater part of the phosphoric acid is thus available for plant food; this being especially the case with basic superphosphate, the whole of whose phosphoric acid is soluble in citric acid solution.

Cheshire Agricultural College,
Holmes Chas. el.

THE SUPPOSED DISCOVERY OF ALUMINIUM TWO THOUSAND YEARS AGO.

THE following letter appears in *Knowledge* for September, 1902:—

SIRS,—The following paragraph appeared in "Echoes of Science" in the *Globe* of August 19th, 1898:—

"The first discoverer of aluminium had the reward of genius. Pliny tells us that in the reign of Tiberius (41 B.C. to 37 A.D.) a worker in metals presented a beautiful metal cup resembling silver, but lighter, to the Emperor, who questioned him, and learned that he had extracted the new metal from clay. The secret, he said, was known but to himself and the gods. The sage Tiberius, reflecting that if this metal could be made from earth it would lower the price of silver and gold, decapitated the artificer in order that his secret might remain with the gods, and so deprived the world of a most useful metal for eighteen centuries."

It would interest many readers of *Knowledge* if some student of Pliny would state where in his works the account is to be found, and furnish a translation thereof.

That the metal of which the cup was formed was really aluminium appears possible from four circumstances:—(1) It was obtained from clay; (2) it resembled silver; (3) it was lighter than silver; (4) it was capable of being wrought into a vessel.

The question naturally occurs, How did the metallurgist of the first century obtain a metal, which in the twentieth century can only be extracted by processes totally unknown to the ancients, and which it is inconceivable that any individual worker among them could have accidentally hit upon? Modern methods of procuring aluminium are:—(1) Chemical, involving the use of sodium or potassium; and (2) electrical. The contemporary of Tiberius cannot have knowingly isolated sodium or potassium, and then applied it to separate aluminium, though it is possible that sodium or potassium may have been liberated from some ingredient of a mixture in his retort or crucible, only to oust aluminium from some other ingredient. That his process was electrical is quite out of the question.

If Pliny's account actually refers to aluminium there must be some method of separating it which modern chemists have failed to light on, but which lay not very far outside of the range of ancient metallurgical knowledge. Cannot it be re-discovered by some chemist possessing a wide knowledge of the science, and who is at the same time well acquainted with the methods (many of them forgotten) adopted by ancient and mediæval workers? Such a process would probably go very far towards cheapening that most useful metal.

JOHN T. KEMP.

Report of "The Lancet" Special Commission on Glycerinated Calf Vaccine Lymphs.—In this report some interesting results of experiments are given concerning the number and nature of the extraneous bacteria found in the commercial vaccine lymphs. We note that there is scarcely a doubt that all the vaccine lymphs at present on the market are, as regards their capability of producing vaccine vesicles, of very trustworthy character at some period or other after their preparation; it is, however, recommended that where any doubt occurs, over-glycerinated rather than under-glycerinated lymph should be used. Many of the cases of bad vaccination are due to either imperfect sterilisation of the skin, or want of protection against the invasion of the weakened and abraded tissues by extraneous organisms. A table giving the results of experiments with sixteen different samples of lymph shows that the numbers of colonies per 0·05 gm. vary from 0 in the case of Merck's lymph to 10,000 in that supplied by Chaumier, and uncountable in the case of that from the "Association for the Supply of Pure Lymph (Darke)" on agar plates.

NOTICES OF BOOKS.

The New Volumes of the Encyclopædia Britannica. The Fifth of the New Volumes, being Vol. XXIX. of the Complete Work. London: *The Times*. Edinburgh: Adam and Charles Black. 1902. Pp. 763.

THE subjects dealt with in this volume of the Encyclopædia, are those comprised between the alphabetical headings GLA (Glarus) and JUT (Jutland).

The first article to attract attention is one on "Glass," by Mr. H. J. Powell. Manufactured glass is classified under three principal headings:—I., Optical Glass; II., Blown Glass; III., Glass Pressed or Blown Mechanically. The author draws attention to the deterioration in the quality of glass articles, owing to the demand by the public for regularity. He says:—

"The beauty of opal glass consists in the wanton irregularity of its shading, no two pieces being precisely similar. The public asked for regularity, and have been supplied with an insipid milk and water material which is called opal. 'Threading' has suffered much in the same way. . . . A lathe has been introduced which not only winds the glass thread with exasperating exactitude, but renders it possible to cover a vessel with threading from top to bottom."

Mr. J. Hays Hammond contributes a short article on Gold, consisting principally of statistics.

The article on Hygiene, by Col. J. Lane Notter, though not very long, is well written and interesting; in it he touches on the influence of soil in the production of disease, the purification of sewage by means of biological treatment, the purification and sterilisation of water, quarantine, plagues, and epidemics.

"Iron and Steel" forms the subject of an important article by Prof. H. M. Howe; the author points out that during the last twenty years the world's production of pig-iron has been more than doubled, and that of steel increased five-fold, the greatest increase being in the United States. Delicate methods of research have revealed the nature and constitution of several varieties of iron; this knowledge has contributed in no small degree to the important beginning which has been made in the use of rational methods of thermal treatment, and it has aided in the discovery and utilisation of numerous "alloy" steels. This article is well illustrated with modern appliances for iron and steel making.

International Catalogue of Scientific Literature. First Annual Issue. D. Chemistry. Vol. II., Part I. Published for the International Council by the Royal Society of London. London: Harrison and Sons. 1902 (June). Pp. 468.

THE possibility of preparing a complete index of current scientific literature by international co-operation was first taken into consideration by the Royal Society about the year 1893, and the Society therefore sought the opinion of a very large number of representative bodies and individuals abroad, the result being that a Conference took place in London on July 14-17, 1896, at which it was unanimously resolved to compile and publish a complete Catalogue of Scientific Literature, arranged according both to subject-matter and author's names, in which regard should be had, in the first instance, to the requirements of scientific investigators, so that these might find out, with a minimum of trouble, what had been published on any particular subject of enquiry.

The supreme control over the Catalogue is vested in an International Convention to be held in London in 1905, 1910, and every tenth year afterwards.

There are seventeen branches of science to be included in the Catalogue, and thus each complete annual issue of the Catalogue will consist of seventeen volumes, and a schedule of classification and an index thereto will be prefixed to each volume in English, French, German, and Italian. The various headings and sub-headings through-

out the subject-index are given in English, and translations of the main headings can be found on reference to the schedules in the other languages by means of the registration numbers that are attached to them.

In the Author's Catalogue each title is given in the original language.

The present volume consists of three parts:—(a) Schedules and Indexes in four languages; (b) An Author's Catalogue; (c) A Subject Catalogue.

The Subject Catalogue is divided into sections, each of which is denoted by a four-figure number between 0000 and 9999. These numbers follow each other in numerical order, but all are not used, as it is intended to fill up the gaps by interpolation of such additional sections as may be required in future years. At the end of the volume a large number of the organic substances referred to in the Subject Catalogue are arranged in alphabetical order; the four-figure numbers given in this list are the registration numbers. In the Author's Catalogue the four-figure numbers in square brackets at the end of each entry are registration numbers.

A large amount of care and thought has been devoted to the compilation of this Catalogue, and it cannot fail to be of great value to scientific men all the world over.

Suggested Standards of Purity for Foods and Drugs. By C. G. MOOR, M.A., F.I.C., F.C.S. London: Baillière, Tindall, and Cox. 1902. Pp. 260.

MANY years ago an attempt was made by the Society of Public Analysts to suggest certain limits or standards as indicating the genuineness of certain articles, such as milk, butter, &c. Some of the figures then suggested are still in use, and the aim of the present work is to endeavour to extend the same principle to other articles that come within the scope of analysts' duties generally, but the figures here suggested must be accepted as tentative only.

With regard to medicinal preparations, the original intention was to deal with all British Pharmacopœial preparations, but as this proved too large a task, a selection had to be made, which led to the omission of most chemicals which either are not likely to be adulterated or for which there are definite chemical tests offering no difficulties.

In considering the merits of any particular article, due regard must be had to the purpose for which it is intended, as there may be a legitimate use for an article which need not be pure in certain cases, whereas if intended for medicinal use its purity would be essential. The book has been carefully compiled, and will be of great assistance to analysts in general.

Hilfsbuch zur Ausführung Chemischer Arbeiten. ("Aids to Practical Chemistry"). By HUGO SCHWANERT. Braunschweig: Friedrich Vieweg und Sohn. 1902.

THIS fourth edition of Dr. Schwanert's "Hilfsbuch" has been considerably enlarged, new methods of separation and determination having been added, while the general arrangement is unaltered. The analysis of inorganic and organic mixtures is very fully treated, and the tables for systematic procedure are particularly good. The section on the preparation of various chemical substances also will be found very useful, the directions being both concise and complete; it might perhaps have been preferable to open the book with this section, deferring the systematic analysis until later. The most important and commonly used methods of gravimetric and volumetric analysis are given (in the latter case very fully); and, finally, the book contains an introduction, by no means superficial, to the analysis of water, food materials, and poisons, together with some experiments in zoo-chemistry, such as the examination of the animal secretions, blood, horn, &c. In the case of milk analysis, the Werner-Schmid method for determining fat is not recommended, although it has been found in practice to be both rapid and accurate.

The General Principles of Physical Science. By ARTHUR A. NOYES. New York: Henry Holt and Co. 1902.

THE author of this book has not succeeded in producing an attractive or eminently readable treatise on the subjects he deals with. Though the style is, on the whole, clear, some parts are decidedly dull, and unlikely to stimulate the reader's interest. Occasionally, statements which are really misleading are made. For instance, the paragraph on specific gravity and density may be cited as likely to lead to confusion in the mind of the student, especially if he had no previous knowledge of the subject. The chapter on the General Principles relating to Matter provides a short treatment of the theory of chemistry; and that on the General Principles relating to Energy, a course of the theory of physics, the second law of energetics being fully discussed. The treatment throughout professes to be entirely non-mathematical, but as some knowledge of the Calculus is assumed, this will probably be of no very great advantage to the ordinary student.

work was dissolved in a liquid metal under great pressure, and cooled. The carbon in my work was also in contact with—and probably dissolved in—liquid metal under great pressure and then cooled. The metal in Moissan's case was iron, and in mine it was potassium and iron; and although my temperature may have been lower, I had proved that there was a violent reaction between the potassium and the contents of the tube, which would raise the temperature locally to as high as Moissan's, and so produce identical conditions, as the carbon was in contact with the iron.

The experiment was planned from discoveries made in my research into the "Solubility of Solids in Gases," and Moissan quotes my paper as the first successful production of crystalline carbon in the diamond form.

Apologising for the length of my explanation.—I am, &c.,

J. B. HANNAY.

Cove Castle, Loch Long, N.B.

CORRESPONDENCE.

ATOMIC WEIGHT STANDARDS AND PROUST'S HYPOTHESIS.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS for September 19 (vol. lxxxvi., p. 147), Mr. Hollins puts forward a view upon the integral nature of atomic weights analogous to that of Proust; but unlike Proust, who made but a superficial generalisation, Mr. Hollins would endeavour to uphold his view by figures calculated to five places of decimals.

To a practical chemist this appears "false accuracy." In the present uncertainty of many atomic weights—even those of the common elements—it appears quite unreasonable to make use of figures taken out to five places when dependent upon figures in which uncertainty appears at least in the second place, and frequently in the integers themselves. There has been a tendency for many atomic weights to fall—as much as two whole numbers in some cases—during the last few years, and we are by no means sure that the numbers now current are final; consequently, it would appear more scientific to make use of figures involving the first place of decimals only. The hypothesis of Proust has at best but doubtful value and bearing upon physical and chemical science, and certainly this value is not enhanced by the use of figures of such fictitious accuracy in its proof.—I am, &c.,

GEO. H. WOOLLATT.

11, Old Park Avenue, Clapham Common, S.W.,
September 22, 1902.

PRODUCTION OF DIAMOND.

To the Editor of the Chemical News.

SIR,—Will you kindly allow me to make a note in your valuable paper on the statement, in the new volumes of the "Encyclopædia Britannica," that the hard substance I found in my tubes was really carborundum (article, "Gems, Artificial")?

Had the original paper or the correspondence in the *Times* been consulted, this could hardly be asserted, as it was fully tested at the time, and was found to be converted entirely into carbon dioxide when burnt in air or oxygen.

But putting that aside, and even the fact that no silicon was used in my experiments, if we accept as a fact (and we all do) that Moissan's carbon was true diamond, then, as the material I made was produced under nearly identical conditions, it is clear that Moissan's experiments really corroborate my result. The carbon in Moissan's

PROPOSED METHOD FOR DETERMINING THE GENUINENESS OF MILK.

To the Editor of the Chemical News.

SIR,—No method, so far as I know, has hitherto been suggested for the discrimination of a milk naturally poor in butter-fat from a rich milk reduced by the addition of separated milk, &c. The obvious advantages that would accrue from the possession of such a method must be my excuse for trespassing on your space at this time with a preliminary note on the result of certain observations and experiments which promise to give assistance in this direction.

Early in my practice as a milk analyst I noticed a seasonal variation in the fatty contents of milk, which reached its maximum in October or November, and had a minimum value about the month of May. This has been recorded by many other observers, and is now well known among those interested in dairy matters.

In the course of similar observations on the composition of butter, I came on a like seasonal variation in the proportion of volatile fatty acids, but having its maximum and minimum points in portions of the year opposite to those in which the maximum and minimum of fat in milk occur.

This variation has been lately put on record by a Dutch observer, whose book was noticed in the CHEMICAL NEWS a short time ago.

Though it is some time since the possibility of a connection between these two phenomena suggested itself to me, it was only lately I had leisure to make the following experiments with a view to finding whether there was any difference as regards volatile fatty acids between the fat of naturally rich and naturally poor milk in favour of the latter. The most crucial case seemed to be that of the morning and evening milk of the same cow, between which there is generally a well-marked difference. Through the kindness of a friend, I obtained a quart each of morning and evening milk from one cow. The cow had calved three months before, and gave in the morning (at 6 a.m.) 2 gallons 4½ pints, and in the evening (at 3 p.m.) 1 gallon 4½ pints. The proportions of fat were—3.20 per cent in the morning and 3.80 per cent in the evening. The two samples were allowed to rest, the greater part of the skim milk drawn off with a syphon, and the cream shaken in the bottle till butter had formed. On estimating the volatile fatty acids in the usual way, 2.5 grms. of fat from the morning milk gave Reichert figures of 14.80 c.c. and 14.85 c.c., while that from the portion naturally richer in fat gave only 14.10 and 14.00.

From this it would appear that there is a distinct inverse relation between the quantity of naturally occurring fat and that of the volatile fatty acids, though the one variation does not completely counterbalance the other; the

fat in the evening milk being only one-twentieth poorer in volatile fatty acids, while one-fifth greater in quantity. Further investigation may, however, furnish sufficient data to enable an opinion to be formed in certain doubtful cases. If, for instance a sample of milk was found poor in fat, and yet the fat was richer in volatile acids than the average for the particular season, this fact would furnish evidence of the genuineness of the milk, for the fat of a rich milk diluted to the same strength would be found to contain less than the average amount of volatile acids.

I trust that dairy chemists who have the opportunity may follow up this question in its various branches.—I am, &c.,

THOS. FARRINGTON, M.A., F.C.S., F.I.C.,
Analyst to the County of Cork
Agricultural Society.

Cork, September 15, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., Nos. 7 and 8, August 19 and 26, 1902.

These two numbers contain no chemical matter.

No. 9, September 1.

Action of Soluble Ferments and of Yeast on Gentibiose. Remarks on the Constitution of Gentianose.—Em. Bourquelot and H. Hérissé.—Up to the present time only two polysaccharides were known which were attacked by invertine; these were saccharose and raffinose. Gentianose is now found to form a third, and recently M. Tanret found a fourth—manneotetrose. In the four cases one molecule of levulose is broken up. The phenomenon has a general aspect, and it seems that it is possible to define it thus:—Only the polysaccharides containing one molecule of levulose united to one molecule of glucose in the same manner as saccharose are attacked by invertine, and that with breaking up of the levulose. To completely hydrolyse gentianose, and probably all the polysaccharides, several ferments are necessary. For a body composed of three molecules there must be two which are invertine and emulsine, or at least a ferment contained in the emulsine of almonds. Further, our experiments show that the actions of fermentation are not simultaneous, that of invertine preceding that of emulsine, since that which hydrolyses biose is without action on triose.

No. 10, September 8.

A New Acidimetric Indicator.—L. J. Simon.—Amongst the products which are formed as an accessory during the calcination of tartaric acid in presence of potassium bisulphate is a new compound, $C_7H_8O_3$, isomeric with pyrotartaric acid, and to which the author assigns the name isopyrotartaric acid. Ferric solutions communicate to an aqueous solution of this an intense violet colouration. This colour is apparently due to the formation of iron isopyrotartarate, a well-defined crystalline compound, $(C_7H_7O_3)_3Fe \cdot 2H_2O$, which serves as an indicator in acidimetric measurements. It has the curious property of giving indications which are usually obtained by the successive use of helianthine and phenolphthalein. The salt, which is very soluble in water, gives it a brownish red tint, nearly black in concentrated solution. On dilution, it becomes orange-red, then reddish yellow. Acids turn this colour to violet in concentrated solution, and to rose in dilute solution. Alkalis, on the contrary, cause a decolouration of the solution to a pale yellow tint.

MISCELLANEOUS.

The South-Western Polytechnic, Chelsea.—This Institute is divided into two distinct portions, day classes and evening classes. The day classes comprise a college for men, a college for women, and a day school for boys and girls. The college for men is at present attended by more than 150 students, whose ages run from sixteen to forty. The courses are arranged to occupy three years. On entering, the student will state whether he wishes to be trained as a mechanical, civil, or electrical engineer, or as a consulting or industrial chemist. In any of these cases he will find mapped out for him a complete course of study, involving laboratory instruction, tutorial work, attendance at lectures, exercises in mathematics, geometrical, mechanical, and architectural drawing, and instruction in the workshops. It is necessary that those who enter for technical instruction should have received previously a sound English education, and have acquired an elementary knowledge of mathematics, and, if possible, of physics and chemistry. The objects of the evening classes are to offer to artisans and others, both men and women, engaged in technical and commercial industries, the means of instruction in applied science and art, and also to women opportunities of training in cookery, dressmaking, and household management; to afford instruction which will be of service to those who intend to enter on a Colonial life, &c. The classes and lectures in technical subjects are designed to supplement, and not to supersede, the training of the workshop.

NOTES AND QUERIES.

Society of Electro-chemists.—Could you inform me if there is in London a Society (or Club) of Electro-chemists, and, if so, where their meetings and reunions are held? Could you also advise me whether there is in London any institution where German chemical papers can be read? I shall be greatly obliged for any information you can give me on these subjects.—Dr. MAX REUTER.

THE DAVY FARADAY RESEARCH LABORATORY OF THE ROYAL INSTITUTION.

Directors:

The Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S.
Professor DEWAR, M.A., LL.D., D.Sc., F.R.S.

Superintendent of the Laboratory:

Dr. ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

This Laboratory was founded by Dr. LUDWIG MOND, F.R.S., as a Memorial of Davy and Faraday, for the purpose of promoting, by original research, the development and extension of Chemical and Physical Science.

MICHAELMAS TERM.—Monday, October 6, to Saturday, December 13.

LENT TERM.—Monday, January 5, to Saturday, April 4.

EASTER TERM.—Monday, April 27, to Saturday, July 25.

Full information and forms of application can be had from the Assistant Secretary, Royal Institution, Albemarle Street, W.

To prevent delay Candidates ought to send in their applications for admission during the course of the Term preceding that in which they wish to enter.

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THE CHEMICAL NEWS.

Vol. LXXXVI., No. 2237.

THE DECOMPOSITION OF UREA.*

By C. E. FAWSITT, Ph.D.

THE author has studied the decomposition of urea into ammonia and carbonic anhydride in aqueous solution at 99° C. as a problem in reaction velocity. The reaction in presence of either acid or alkali would be expected theoretically to be bi- or tri-molecular, but the experimental results show that in these cases, and also when pure water is used as the solvent, decomposition proceeds in accordance with the formula of a mono-molecular reaction. This apparent anomaly is explained by assuming the formation of an intermediate product, namely, of ammonium cyanate; further, the presence of this salt in the solution, as an intermediate product and not as a by-product, has been proved.

COLLOIDS OF ZIRCONIUM, COMPARED WITH THOSE OF OTHER METALS OF THE FOURTH GROUP.*

By Dr. J. H. GLADSTONE, F.R.S.,
and
WALTER HIBBERT, F.I.C.

ON continuing the experiments on colloids, which were described in their papers at Dover and Glasgow, the

that have previously been observed in solutions of silicon. All these colloids seem to be marked by the extreme readiness with which the hydroxyl element replaces more or less chlorine, and by the number of molecules of water with which they will combine.

ISOMORPHOUS SULPHONIC DERIVATIVES OF BENZENE.*

THE crystallographic study of the 1:3:5 series, the *second* of the three series of sulphonic chlorides and bromides to be derived from the 1:3-dichloro-, chlorobromo-, and dibromo-benzenes examined thus far, has been practically completed by Dr. Jee during the past year. The results are even more striking than those obtained in the case of the 1:3:4-series, as there is evidence that the compounds constitute not merely an *isotrimorphous* group, as in the latter case, but an *isotetramorphous* group, as shown in the accompanying table.

In this series the dibromobenzenesulphobromide has again been the means of formulating the relationships between the various terms, having been obtained in two distinct polymorphic forms. But in comparison with the 1:3:4 series the order of stability is reversed, the transition temperature becoming lower in passing down the series.

It is proposed to submit an account of the results obtained in the case of the 1:4:2(SO₃H), 1:3:4(SO₃H), and 1:3:5(SO₃H) series to the Royal Society in the autumn.

	Orientation.			Crystallographic systems.			
	1.	3.	5.	Anorthic.	Monosym.	Monosym.	Anorthic.
1.	Cl	Cl	SO ₂ Br	Stable	Stable	—	—
2.	Cl	Br	SO ₂ Br	—	Stable	—	—
3.	Br	Br	SO ₂ Br	—	Stable	Labile	—
4.	Br	Br	SO ₂ Cl	—	—	Stable	—
5.	Br	Cl	SO ₂ Cl	—	—	Stable	—
6.	Cl	Cl	SO ₂ Cl	—	—	—	Stable
				α-Series	β-Series	γ-Series	δ-Series

authors found that zirconium gave a colloid of well-marked properties, resembling those of silicon, tin, titanium, and thorium. The tetrachloride of zirconium is a volatile pungent body which, reacting with water, forms hydrochloric acid and various oxychlorides or hydroxides. The gummy mass so obtained, when dried, gave beautifully regular forms of fissures and spirals. The gummy solution, when heated, formed a gel which, when exposed to the air, gradually lost water. Successive diffusates from this gel gave various crystalline forms on evaporation. The first diffusate was particularly rich in dagger-shaped crystals with rounded edges, which proved to be oxychlorides. In later diffusates this compound was gradually replaced by crystals of other forms, similar to what had been previously observed among the colloids of tin and titanium, and which appeared to be free from chlorine. These crystals were extremely labile, and exhibited forms always more or less curved in their outlines. The solutions of these colloids of zirconium, tin, and titanium slowly formed crusts or skins which were insoluble in water, and which slowly shrank, often cracking in irregular patterns. It is a curious circumstance that the solution of zirconium colloid very readily produces spongy growths, similar in appearance to those

The third series of the 1:3 derivatives, in which the sulphonic group is between the halogens, has yet to be examined. Very great difficulty has been experienced in preparing the necessary material, but methods have now been devised which promise success. Thus diorthobromobenzenesulphonic acid has been prepared from diorthobromaniline by Gattermann's sulphinic acid method. Unfortunately, the corresponding dichlor- and chlorobromanilines are not at present available, and therefore other methods of preparing the dichlor- and chlorobromacid need to be devised. Apparently these will be obtainable from the dimeta-derivatives of aniline.

A complete series of 1:2:4(SO₃H) derivatives has been prepared, and their crystallographic study will now be undertaken. To complete the investigation, so that it shall comprise all the series derivable from the dichloro-, dibromo-, and chlorobromo-benzenes, only the 1:2:3(SO₃H) series has to be prepared. This, again, is a matter of considerable difficulty, requiring special investigation.

Progress has been made in extending the investigation to the comparison of the effect produced by homologous hydrocarbon radicles, and also in contrasting corresponding sulphur and oxygen compounds.

* Read before the British Association (Section B), Belfast Meeting, 1902.

* Thrd Report of the Committee, consisting of Professor H. A. Miers (Chairman), Dr. W. P. Wynne, Mr. W. J. Pope, and Dr. H. E. Armstrong (Secretary). Drawn up by the Secretary. Read before the British Association (Section B), Belfast Meeting, 1902.

ON FLUORESCENT AND PHOSPHORESCENT
DIAMONDS.*

By Dr. J. H. GLADSTONE, F.R.S.

IN the *Comptes Rendus* of the French Academy of May 20 last there is a short communication by M. Chaumet on the action of light on precious stones, in which he describes the fluorescence excited in some diamonds by violet light, and mentions the case of a yellow diamond which showed no fluorescence under those rays, but after a few minutes' exposure became dark brown; after twenty-four hours, however, its original colour and brilliancy returned.

This reminded me of the diamond ring which I exhibited at the meeting of the British Association at Aberdeen in 1859, containing five stones, two of which were strongly fluorescent in sunshine and one slightly so, while the other two did not exhibit that property. These fluorescent diamonds continued to phosphoresce for some hours in the dark (see *Brit. Assoc. Report*, 1859, Trans. Section B, p. 69). The phenomenon was afterwards exhibited by the Rev. Dr. Robinson at the evening lecture. A few days later, when on a visit to a friend who had a remarkably fine collection of jewellery, I had the opportunity of examining her diamonds in the sunshine, but not one of them showed the least trace of fluorescence. I concluded, therefore, that diamonds of the first water did not possess this property. Possibly the fluorescence in the three diamonds of the ring may have depended upon some impurity. It was found subsequently that they shone most brightly when exposed to the violet and ultra-violet rays. A long exposure to sunlight, however, exhausted the power of phosphorescence for a time, but this was not due to any increase of temperature.

In 1896, Prof. Silvanus Thompson exhibited the ring during the course of his lecture on electric shadows and luminescence at the Royal Institution. The diamonds shone very brilliantly, but next day it appeared they had entirely lost their phosphorescent power. They were kept in the dark, and when examined a few months afterwards it was found that the power of phosphorescing was restored, though not to its former extent.

M. Chaumet says that all diamonds, whatever their quality, exhibit the same transparency to the X-rays. I happen to possess a radiograph of the ring, taken in January, 1897; it shows a slight amount of absorption by all the five diamonds, in strong contrast to the great absorption of the gold setting; and there is no discernible difference between the diamonds that fluoresce and those that do not. According to Sir William Crookes, the absorption of the X-rays by the colourless diamond and by the black form of carbon are alike.

Unfortunately, the experiment with these diamonds cannot be continued, as they were lost when my luggage was accidentally destroyed by fire when travelling through Belgium.

THE NATURE OF ALLOYS.†

THE research for which this Committee was formed is completed, and a summary of the results has been published in the *Proceedings of the Royal Society*, vol. lxi., p. 320. A copy of this paper has been sent to the Secretary of the British Association.

The work consists in a study of the chemical compounds and solid solutions to be found in alloys composed of copper and tin.

At least three series of solid solutions are formed during the solidification of these alloys.

The first series, which may be called Alpha, consists of crystals, isomorphous with pure copper, and varying in composition from pure copper to an alloy containing about 9 per cent by weight of tin. These alloys solidify to a uniform mass, and apparently remain unchanged at all lower temperatures.

The second series, which may be called Beta, contains percentages of tin varying from 22·5 per cent to 32 per cent. Alloys between 9 per cent and 22·5 per cent of tin solidify as a complex of crystals of Alpha and of Beta. But all the alloys from 9 per cent to 32 per cent of tin undergo important re-crystallisations after they have wholly solidified, and their final condition below 500° C. is that of a complex of Alpha and a crystalline body which is probably Cu_3Sn .

Alloys from 32 per cent of tin to 57 per cent begin to solidify by the formation of a third type of crystalline solid solutions, which may be called Gamma. But the Gamma crystals break up at lower temperatures into a complex of crystals of the body Cu_3Sn and another substance. The alloy of the formula Cu_3Sn is apparently a solid solution when first solidified, and is not converted into the compound until a lower temperature is reached.

Gamma crystals containing more than 41 per cent of tin have the peculiarity that, in cooling, they break up into solid Cu_3Sn and a liquid. Between 57 per cent of tin and 93 per cent, the first solid that forms when the liquid alloy begins to solidify consists of crystals of Cu_3Sn ; but when the temperature falls to 400° C., these crystals become unstable, and a reaction takes place between them and the liquid, which results in their partial transformation into a body that is nearly, or quite, pure CuSn . Between 93 per cent and 99 per cent of tin the substance CuSn is the first body formed during solidification. Between 99 per cent and 100 per cent tin appears to crystallise first.

Assuming the alloys to have been cooled with sufficient slowness, we may summarise their condition at ordinary temperatures as follows:—

0 to 9 per Cent of Tin.—A uniform solid solution (Alpha) of copper containing tin, or, more probably, containing a compound, in solution.

9 to 25·5 per Cent of Tin.—A complex of large crystals of Alpha in a minute eutectic of Alpha and Cu_4Sn .

25·5 to 32 per Cent of Tin.—The same complex, but containing the Cu_3Sn in the larger crystals, and the Alpha only in the minute eutectic. At 32 per cent the alloy is pure Cu_4Sn .

32 to 38·5 per Cent of Tin.—A complex of Cu_4Sn and Cu_3Sn , or of two solid solutions of these substances. At 38·5 per cent the alloy is pure Cu_3Sn .

38·5 to 93 per Cent of Tin.—Large crystalline plates of Cu_3Sn coated with a body that is almost pure CuSn , the whole being immersed in a eutectic of this body and tin.

93 to 99 per Cent of Tin.—Large crystals of CuSn in a eutectic of this body and tin.

99 to 100 per Cent of Tin.—Large crystals of tin in the same eutectic.

STATISTICS CONCERNING THE TRAINING OF
CHEMISTS EMPLOYED IN ENGLISH
CHEMICAL INDUSTRIES.*

THE Committee decided that the best method of obtaining the desired statistics concerning the training of the chemists employed in English chemical industries was to send a circular-letter, with a form for reply enclosed, to all those members of the Society of Chemical Industry

* Read before the British Association (Section B), Belfast Meeting, 1902.

† Report of the Committee, consisting of Mr. F. H. Neville (Chairman and Secretary), Mr. C. T. Heycock, and Mr. E. H. Griffiths.

* Report of the Committee, consisting of Professor W. H. Perkin (Chairman), Professor H. E. Armstrong, Mr. G. T. Beilby, and Professor G. G. Henderson (Secretary).

who, so far as could be judged from the designations given in the list of members, occupy a position as manager or chemist in a works. This method was adopted because the great majority of the chemists engaged in technological work in this country are members of that Society, and because no other means of obtaining the information seemed practicable. The result of the inquiry was that more than half of those addressed sent replies to the circular. It is probable that a considerable proportion of those who did not reply are not engaged in chemical works, and therefore the accompanying statistics may be considered to give a fair idea of the present position.

Information concerning their course of training was received from 502 managers and chemists employed in English chemical industries. Of these, 107, or 21 per cent, are graduates, and 395 have not taken a degree; 111, or 22 per cent, are Fellows or Associates of the Institute of Chemistry.

The following figures give more detailed information:—

Number of graduates of a British university	59
Number of graduates of both a British and a foreign university	16
Number of graduates of a foreign university	32 (a)
	107
Number of non-graduates trained in a British university or university college ..	137 (b)
Number of non-graduates trained in a British technical college	165
Number of non-graduates trained in a foreign university or technical college ..	8
Number of non-graduates trained in evening classes, analysts' laboratories, works' laboratories, or otherwise	85
	395

(a) Thirteen of whom studied also in a British university or technical college.

(b) Twenty of whom studied also in a foreign university or technical college.

The distribution of the chemists among the principal industries is shown in the accompanying table.

THE PROPOSED STANDARDISATION OF METHODS OF CHEMICAL ANALYSIS.*

By BERTRAM BLOUNT, F.I.C., F.C.S.

THERE has been evident of late years a tendency to apply the principle of standardisation to matters and in directions differing considerably from those in which the advisability of erecting and enforcing a standard is generally conceded.

The commonest examples of standardisation, namely, those of weights, of measures, and of money, have come into existence and are maintained by their manifest necessity. The standardisation of such things as gauges for wire and sheet, of screw threads, and the like, is also desirable. But there are limitations to the usefulness of standards, and these are reached when it is proposed to standardise sections of structural metals, sizes of test-pieces for mechanical tests, and methods of applying such tests. Whether these are to be standardised or not is largely a matter of convenience and expediency.

In mechanical testing it is recognised that the values obtained for strength in tension and compression, for elongation of a ductile test-piece, for resistance to shock and the like, are appreciably influenced by the conditions of the test, and in consequence there is something to be said in favour of standard methods of applying the tests. But there is no such justification for the adoption of standard methods in chemical analysis where the object in view is the determination in a given material of a definite substance; in such a case all methods which are chemically sound must give the same result.

But notwithstanding these obvious facts a desire has arisen in some quarters for the formulation of standard methods of chemical analysis and for their gradual imposition on the community of chemists; steps have been taken to secure this end, and it is necessary to decide whether this movement is laudable or not lest judgment should go by default.

The wish to establish standard methods of analysis is no new thing. From time to time propositions to this end have been put forward, but they have led to little result in this country. In America, however, they have been

* Abstract of a Paper read before the British Association (Section B), Belfast Meeting, 1902.

Industry.	Graduates—			Non-graduates, trained in—				Total.
	Of British university.	Of British and foreign university.	Of foreign university.	University or technical college.	Technical college.	Foreign university or technical college.	Evening classes, &c.	
Acids, alkalis, inorganic salts	9	3	5	20	19	2	20	78
Metallurgical (various)	1	—	4	19	13	—	14	51
Explosives	6	—	1	4	28	1	6	46
Dyeing and printing	3	—	—	13	16	—	5	37
Oils, fats, soaps, candles	2	1	3	11	9	1	5	32
Colours, pigments, oils, varnishes	8	1	2	6	5	—	6	28
Brewing and distilling	3	—	4	8	12	—	1	28
Fine chemicals, pharmaceuticals, confections	7	—	—	9	6	—	4	26
Sugar, starch, glucose	3	2	1	2	8	—	3	19
Cement, tiles, pottery	—	1	1	5	10	—	1	18
Aniline colours	2	3	7	2	2	1	—	17
Tar distilling	—	—	—	5	8	—	3	16
Paper, paper-pulp	—	—	2	3	3	—	—	8
Glue, gelatin, size	—	1	—	4	2	—	—	7
Paraffin and paraffin-oil	—	—	—	3	4	—	—	7
Dyewood and tanning extracts	—	—	—	5	2	—	—	7
Cyanides and ferrocyanides	3	1	—	—	2	—	—	6
Glass	2	—	—	2	1	—	1	6
Coal-gas	—	1	—	—	3	—	2	6
Miscellaneous	10	2	2	16	12	3	14	59
Total	59	16	32	137	165	8	85	502

more favourably received, and standardisation of analytical methods for a number of materials has been advocated. Quite recently (in 1901), a committee of the New York Section of the Society of Chemical Industry approached the same subject in the same spirit, and has reported in favour of a standard method of analysis for cement and cement materials. I had the honour in May last of reading a paper before this body, in which I ventured to criticise the method in detail, and to dissent from the acceptance of a standard method.

It may be accepted that there is an increasing tendency to propose standardisation of analytical methods irrespective of the nature of the material to be analysed, and it remains to consider how this tendency has arisen and what effect it is likely to have if it continues to grow without opposition.

In the first place it will be seen that there are in this matter two schools of thought sharply differentiated. On the one hand, we have chemists so impressed with the necessity of avoiding discrepancies that they are anxious to set up standard methods stated in such detail that a faithful observance of the prescriptions by two workers cannot fail to secure identical results. And there are others less confident of the success of this system. This conflict of opinion arises in great measure from confusion of thought. There are many operations performed by the chemist which are from their nature arbitrary. To take an extreme case, it is evidently impossible to carry out the Maumené test for oils, or to determine the flashing-point of petroleum, and to obtain concordant results without having recourse to a fixed procedure. In the examination of potable waters such arbitrary methods are in wide and general employment, and yield much useful information. Feeding-stuffs and manures afford a similar case. "Citrate-soluble phosphoric acid" is a meaningless term unless the conditions of its extraction are laid down. The fractional distillation of crude benzol and the return of its computed contents of benzene is another instance.

But this sort of codification, though useful and often necessary, has nothing to do with analysis. The object of the analyst is to determine with the best precision in his power the constituents of the substance which he is analysing. Sometimes he cannot do this, and is forced to have recourse to the determination of the properties of the substance; that is to say, he is compelled to apply to the material under examination various arbitrary tests. Standardisation for these tests is legitimate enough; standardisation of analysis implies that analysis is an arbitrary procedure not based on ultimate chemical facts; this view is too grotesque for discussion.

To turn to the much debated question of discrepancies in analytical results which is at the root of the whole matter.

In trade it is necessary frequently to appeal to the analyst, and if the results given by one analyst differ from those of another examining what is believed to be the same sample, much delay and expense may be incurred. The trader is usually unaware of the great difficulty which exists in procuring identical samples, and he is almost certainly ignorant of the slow and laborious character of all analytical processes having claim to be exact. From the former cause he is disposed to ascribe all differences to errors of the analyst, and from the latter he is inclined to urge greater rapidity of work than is compatible with accuracy. Sometimes from bad sampling or from hurried or unskilful work discordant or erroneous results may arise. Then the trader seeks a remedy, and believes that it may be found in a standard method of analysis. It is obvious that such a conclusion is fallacious. The same imperfection in sampling, the same hurried and unskilful work, will lead to the same erroneous results.

It is not likely that chemists who practice as independent consultants will submit to dictation even from a committee of their peers as to the methods they are to employ. A member of this branch of the profession asked to determine in some material a definite constituent is

either competent to choose a suitable method and to execute it accurately or he is not. If he is, a standard method is superfluous; if he is not, his early retirement is desirable and will probably occur from the operation of natural causes. But there are some consultants who are more or less identified with particular branches of the chemical trade—they are constantly called upon to carry out analyses or assays for the buyers and sellers of ores, metals, minerals, salts, and the like, and usually the results obtained by the buyer's and the seller's chemist are compared, and may be found to disagree.

Now here is a plausible case for the use of a standard method. It is argued that if the two chemists concerned were to use the same process, the likelihood of their disagreement would be diminished. There is even a limited truth in this; the likelihood of disagreement would be diminished to some extent because both operators would be exposed to identical chances of error instead of different chances. But the object of analysis is not to obtain a false concord by repeating a process, errors and all, with Chinese fidelity; it is to arrive at the truth as closely as knowledge and skill will allow, and one of the recognised methods of doing this is to vary the conditions of experiment.

A great part of the clamour for standardisation arises from the discrepancies which often occur between the results of different works chemists, and it appears that the "standard" methods, which have from time to time been proposed in the United States have the works chemist as their particular objective. These discrepancies are highly inconvenient, not only immediately to those concerned, but ultimately as tending to discredit the value of analytical control of manufacturing processes. When last in America I took some pains to ascertain the opinion of chemists on this point, and found that those who advocated the adoption of standard methods when confronted with the grave objections which can be urged against them, took refuge in the necessities of the works chemist, maintaining that only by the provision for him of standard methods could uniformity and accuracy be attained.

It cannot be denied that this view is defensible, but it is defensible on one ground alone, and that hardly likely to commend itself to the works chemist. His friends, in their anxiety to help him, infer that he is incompetent and needs to be guarded and guided like a schoolboy. Now, as a matter of fact, although often overburdened with work and most inadequately paid, the works chemist has done much to advance analytical chemistry, originating some methods and improving many others. It is neither just nor courteous to assert that he above all others is in need of direction and supervision from without, and that he is willing to barter his right of individual judgment according to his training and experience for a bundle of prescriptions. If, as is sometimes unfortunately the case, the works chemist is conscious of deficiencies, and welcomes "standard" methods, an argument is provided, not for the use of standard methods, but for the employment of better trained men. The fault is the manufacturer's, who hopes to obtain a chemist at the wages of a mechanic.

There are other results to be expected of wider and more general importance. Let us suppose that standard methods have been prepared and published with the consent, and under the direction of, some body of chemists of sufficient standing to make their pronouncements authoritative. The position of all chemists who ventured to disagree with the findings of this central body would become very difficult. In all cases of dispute, in all legal proceedings, these dissentients would be placed at a disadvantage; on them would be thrown the onus of proving, usually before a non-technical tribunal, that the method they preferred was as good as that of the central committee. If the dissentient were not able to convince the lay tribunal that his process was reliable a grave injustice might be done to him; if, on the other hand, he did so

succeed the standard process would be discredited. A whole vista of trouble and dispute can be foreseen. The endeavour here made to trace to its logical outcome the effect of standardisation is sufficient to show that such a scheme, even if it could be regarded as desirable, would lead to such complications as to render it impracticable.

But there are still further drawbacks of a kind yet more serious. If a standard process is adopted by a central authority it will be regarded by many as final, and all incentive to original inquiry in that direction will be removed. The deviser of a method radically different from that which is official will be regarded as a sort of chemical heretic, and will receive the treatment usually accorded to the heterodox. Now, analytical research, although not the highest form of chemical investigation, is of great value, both as a school of training and as a means of perfecting the chief instrument of the chemist, whose work, unless constantly controlled by its aid, would be little better than a maze of ingenious speculation. Anything calculated to discourage the criticism of existing analytical methods and the device of new ones is therefore much to be deprecated.

There is too good a case against the standardisation of methods of chemical analysis to make elaboration of argument necessary or wealth of instance and illustration desirable. The plain facts constitute so crushing an indictment, and appeal so strongly to every thinking chemist who is jealous of the dignity of his chosen profession, that their statement without ornament or rhetoric must suffice for conviction. But as there is nevertheless a respectable body of opinion in the contrary sense, it may not be superfluous to register a formal pronouncement that standardisation is undesirable except in cases where arbitrary methods of examination cannot be avoided.

Something may be done towards the construction of a positive policy. Revision of analytical methods is certainly desirable. This should be undertaken by committees of specialists acting under some central body, whose business it should be to examine and report on established and on new methods of analysis, each committee dealing with one of the great branches of technical analysis. The function of these committees would be critical and advisory, and no attempt would be made to erect a standard method. The object aimed at would be to ensure that the methods examined and finally approved should be at once reliable and practicable. In this way real analytical progress would be effected.

It will be seen that the programme suggested differs radically from that to which I have ventured to take exception. The latter involves the pronouncement of a defined method for the determination of a given substance; the former is directed to the discovery of latent errors and to the provision of processes free from these. In the one case, a set of rules is imposed from without; in the other, advance and improvement will take place from within, unfettered by canon and unhampered by rule. I think it not too much to say that the whole spirit of science, which is instinct with the love of freedom and the defiance of mere authority, will be found favourable to the plan which I have put forward, and will unconditionally condemn any attempt to standardise methods of chemical analysis.

Action of Hypochlorous Acid on the Metallic Chlorides.—W. van Tiesenholt.—The author describes several experiments which prove the production of free alkali in the decomposition of alkaline chlorides by hypochlorous acid according to the equation $\text{KCl} + \text{ClOH} = \text{KOH} + 2\text{Cl}$, which it can be seen is nothing but the inverse of the equation for the formation of hypochlorites. Experiments were also made on other chlorides, and especially the chlorides of the alkaline earths; the author draws some conclusions from his experiments, relative to the formula of chloride of lime and some of its reactions.—*Journ. f. Prakt. Chem.*, [2], vol. lxiii, p. 30.

DETECTION AND APPROXIMATE ESTIMATION OF MINUTE QUANTITIES OF ARSENIC IN BEER, BREWING MATERIALS, AND FOOD-STUFFS.*

By WILLIAM THOMSON, F.I.C.

SINCE the arsenic in beer scare at the end of 1900 various methods, chiefly modifications of known processes, have been devised for the detection and estimation of minute quantities of arsenic in beer, malt, and other articles of food.

In London the Society of Chemical Industry formed a Committee for devising a standard or official method of testing for and estimating arsenic, whilst the Manchester section of the Society of Chemical Industry did the same thing.

It is impossible for a committee of this kind to work effectively. There is no sum of money placed at its disposal, and, as the devising of a standard method means the making of hundreds of experiments at a large expenditure of time and money, the members of such a committee, if they perform the duties of the office, will find the post no sinecure, and even if a process be formulated by such a committee it should not be suggested as final, but should be submitted to the most stringent criticism from chemists all over the world. The requirements of such a process are:—

1. That the results be obtained quickly,
2. That the personal equation should, as far as possible, be eliminated, so that two chemists would obtain as nearly as possible the same result when working on the same sample,
3. That as it yet remains uncertain as to how much arsenic may be taken without injury to health, cognisance should be taken of very minute quantities of arsenic up to, say, the $\frac{1}{10000}$ th of a grain of arsenic trioxide per lb. avoirdupois of solid or per gallon of liquid.

There are many methods by which the presence of arsenic may be detected:—

First.—The arsenic may be precipitated from beer or from water or acid solutions by sulphuretted hydrogen, and then treated by a variety of methods for its final determination. If the final precipitate be weighed, very large quantities of the material must be taken, and I think when an article contains the $\frac{1}{10000}$ th to the $\frac{1}{100000}$ th of a grain per lb. of solid or per gallon of liquid of the trioxide, that all will agree that the weighing method is not admissible, because these quantities are beyond the limits of direct gravimetric determination even when large quantities of the article are used for the analyses—and such are not usually available.

Second.—There are tests depending on volumetric determination, and in this we have a more accurate method than in the gravimetric. In this the arsenic liberated as arseniuretted hydrogen is passed into silver nitrate solution, and the precipitated silver determined volumetrically, or the arsenious acid left in the solution may be determined volumetrically, or, lastly, the metallic silver, which amounts to about six times the weight of the arsenic required for its precipitation, may be weighed and the weight of arsenic calculated therefrom, but when we are dealing with such minute quantities as the $\frac{1}{10000}$ th of a grain per gallon as a maximum, all these processes are inadmissible.

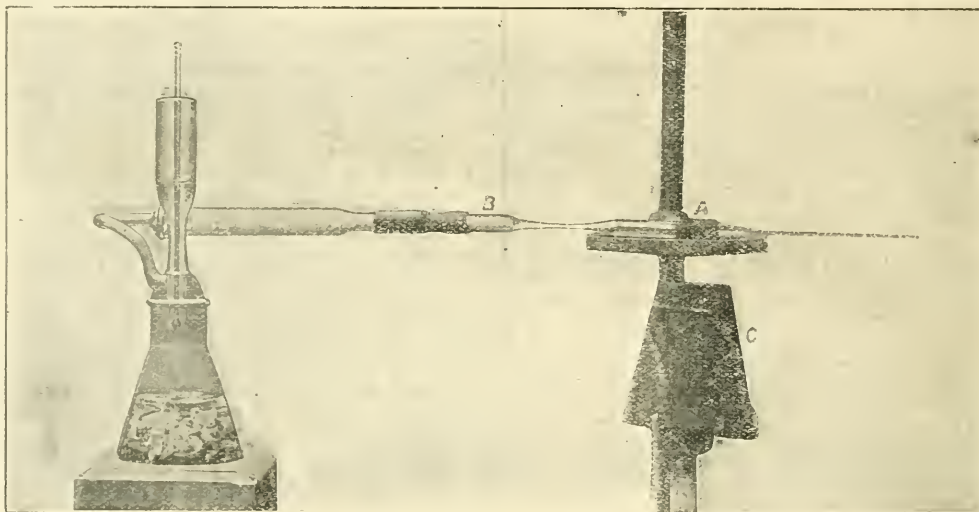
Third.—There are the tests depending upon the intensity of the colour obtained from deposits of arsenic as such, or of some chemical combination thereof, or of some other compound produced by the arsenic.

In this case we have the Gutzeit and the nitrate of silver tests.

* Read before the Manchester Section of the Society of Chemical Industry, May 2, 1902.

After experimenting for some months with these two processes I have thrown them aside as impossible, the extent of these deposits or colours being influenced by so many conditions. It appeared to me at one time that I had obtained in the Gutzeit test a good one for approximately determining minute quantities of arsenic. It was found necessary in order to obtain the fine canary-yellow colour of the mercury compound that oxygen should be present, and I suspended fine sewing threads through glass tubes of very narrow bore, and for different quantities of arsenic present I obtained different lengths of the thread coloured to about the same intensity, and although this seemed at first to give relatively good estimates of the quantities present, I soon found that the results were so irregular and different that I had to discard it; and after trying blotting-paper containing mercuric chloride over the top of the generating flask, this process I also discarded as inadmissible.

I arrived at the same conclusion when using silver nitrate on sewing threads and on paper in the dark. The results seemed more delicate than with the mercuric chloride in the Gutzeit test, but here again the results were so unsatisfactory and irregular that I also discarded this process.



I have made many experiments with Reinsch's test for the purpose of determining minute quantities of arsenic by depositing the arsenic on copper, and then heating the copper strips gently in small glass tubes, and comparing the densities of the white sublimes, but this process I found to be quite untrustworthy.

Experiments were made to measure the volume of the precipitate of mercury and of the metallic silver in tubes drawn out to a very narrow bore, but these also proved unsatisfactory, and the only one left which showed satisfactory results was the Marsh-Berzelius test. I have spent a great part of the last eighteen months in a research to discover the conditions required for giving the most reliable and accurate estimations of minute quantities of arsenic in malt, beer, and other articles of food by it.

A Joint Committee of the Society of Chemical Industry (London Branch) and of the Society of Public Analysts has already made a report with a view of formulating a standard method for detecting the presence of arsenic and approximately determining the quantity, and I propose to take the order of treatment which they have adopted for the purpose of criticism, because no process can be regarded as a standard till it has passed successfully through this ordeal. I appreciate fully the valuable work which some of the members of this committee have done,

especially in their attempt to found a standard process of analysis, and I propose as my contribution to the work to offer my criticism, differing from them where I must, and agreeing with them where I find it possible. I will take the order in which they present their report:—

Materials Required.

Hydrochloric Acid.—I agree that the acid sold as pure nearly always, if not always, contains arsenic.

The Joint Committee propose to purify that "pure" acid by diluting it to 1.10 specific gravity, then adding to it about 5 c.c. of bromine per litre of acid. Then sulphurous acid is added in excess; or hydrobromic and sulphurous acid may be added, and the mixture allowed to stand for twelve hours. This seems to me an extraordinary proceeding which requires explanation. What is the object of the bromine or hydrobromic acid? No satisfactory explanation is given. However, that procedure matters little so long as the required result can be obtained.

The acid is then boiled till about one-fifth has evaporated, and the residue can either be used direct or may be distilled, the whole of the arsenic having volatilised with the first portion of liquid which was boiled off.

I have carried out this procedure exactly as given, and after evaporating a fifth of the liquid I found that the arsenic had not been removed from the residue, and on continuing the distillation I found the further distillate to contain arsenic. This is unfortunate for the standard process devised by the committee.

My method of purifying hydrochloric acid is a very simple one. I do not require to use the purest acid which can be bought to start with. I simply dilute strong acid of any kind with about one-third its volume of water, although the dilution is not necessary. (If the acid be not diluted some water must be put in the receiver to condense or dissolve the HCl liberated as a gas at first). I put it in a retort, add to it about 1 grm. per litre of chromic acid, and distil. By preference I use a large stoppered glass flask placed on a sand-bath, a tube from the neck of which enters a Liebig's condenser, glass touching glass, and the distillate is collected. It is, however, saturated with chlorine.

I then pass a current of filtered air through the distillate, say about half a gallon, for about two hours by means of a water vacuum pump, when every trace of chlorine is removed, and no trace of arsenic will be found in the distillate.

On standing in most glass bottles hydrochloric acid

becomes faintly contaminated with arsenic, but the amount does not exceed the $\frac{1}{1000}$ th of a grain per gallon dissolved during one month.

Sulphuric Acid.—The Joint Committee say sulphuric acid is more frequently obtained arsenic-free than hydrochloric acid. My experience has been very different from this, for I purchased sulphuric acid wherever I was told it was to be found pure all over the country, but I never obtained till very recently a sample of acid which was even approximately arsenic-free. Mr. Hart, of Messrs. Tennants and Co., of Manchester, sent me a sample which was practically free from arsenic, but it did give the shade of a mirror from 10 c.c., and it was therefore not absolutely free from arsenic.

The process given by the committee for purifying sulphuric acid is to take half a litre "pure for analysis" and add to it a few grammes of sodium chloride and distil from a non-tubulated glass retort, the first portion of 50 c.c. being rejected. This process I find also to give sulphuric acid free from arsenic, but the process is not a nice one to carry out. Hydrochloric acid vapours are copiously evolved, and if the acid contain any sulphurous acid, that objectionable body is not removed, and the result is that white sulphur mirrors are obtained by the use of the so-called purified acid.

The method I employ is, I think, much simpler than this, and deals with any sulphuric acid, whether "pure for analysis" or crude from the manufacturer.

Into a non-tubulated retort I put the sulphuric acid previously mixed with about a gramme to the litre of chromic acid or potassium permanganate. I distil and collect the distillate, which is free from any trace of arsenic or from sulphurous acid. If the tube of the retort has been contaminated with the crude acid during the process of filling, I throw away the first portion of the distillate. It is best to fill the retort with crude acid by means of a funnel and long glass tube, near the end of which is fixed a small section of bored cork to prevent the liquid at the end of the tube from touching the neck or tube of the retort when withdrawing the filling tube. The retort is set in a sand-bath standing on a ring burner, with an iron tray underneath, contained in a wooden box, and the neck of the retort passes through a hole in the end of the box; the top of the retort is covered with asbestos cloth, but not the tube. If the tube be covered all the way down it is liable to break suddenly from the end, the breakage running up towards the retort, and this produces an objectionable evolution of acid vapour into the laboratory. If the retort should break, the gas can be turned off from the outside, the lid placed quickly on the box, and a wet cloth thrown completely over it, which avoids any nuisance.

The whole of the distillate, even if the distillation be carried nearly to dryness, is free from any trace of arsenic.

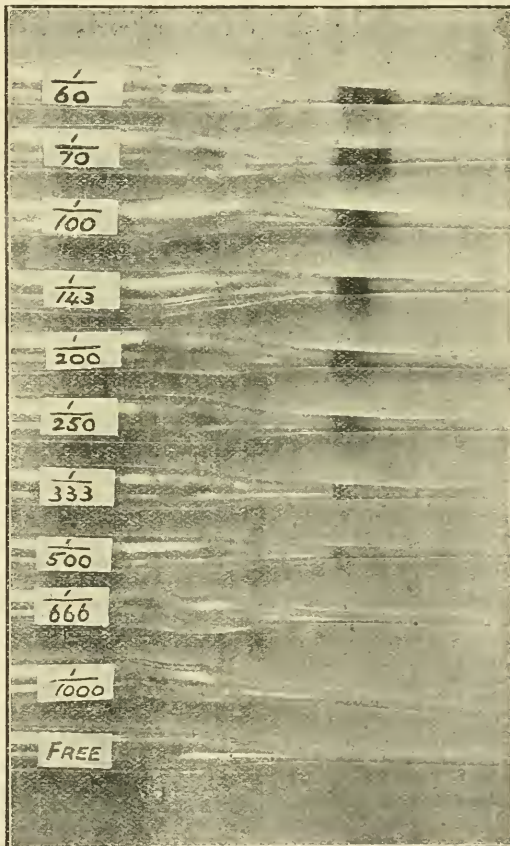
Nitric Acid.—The Joint Committee say this acid can, "as a rule," be obtained free from arsenic. I have never found any of the ordinary re-distilled nitric acid which I purchased from the dealers, except one, to contain any trace of arsenic, but it is advisable to make blank tests to prove that it is free. The one in question showed only the faintest trace.

Zinc.—The Joint Committee say that arsenic-free zinc is obtainable from chemical dealers. My experience has been that out of five or six samples sent by dealers as arsenic-free one is actually so. The zinc employed should be so pure that when placed in dilute sulphuric or hydrochloric acid very little hydrogen is liberated.

I find it necessary to add a little sulphate of copper to start and carry on the reaction. If the reaction commences at once vigorously the zinc contains some foreign metal, such as iron, in sufficient quantity to hold back considerable quantities of arsenic, so that although it may give hydrogen free from arseniuretted hydrogen it is yet quite unsuitable for the Marsh test.

It would be well if a reliable supply of zinc could be obtained free from iron or arsenic, and there seems no

reason why such should not be obtained electrolytically. Samples of electrolytic zinc which I have obtained yield no arsenic mirrors, but are contaminated with iron to such an extent as to be useless. If, however, this zinc be treated with acid, some pieces, especially those which have granulated in button form, produce rapid effervescence, and become black on the surface, from the formation of a deposit of metallic iron, whilst other parts, especially those which are most feathery, yield very little effervescence, and it is easy thus to pick out the good from the bad. The feathery pieces, being usually free from both arsenic and iron, are suitable for the Marsh test. I suggested to one manufacturer of electrolytic zinc that as the zinc was deposited on iron rollers the part furthest from the iron might be turned off on a lathe and sold to the pure-chemical manufacturers, but they did not see their way



to do this. Mr. Allen suggests that the zinc should be contaminated with a trace of iron to get it to work; this may be satisfactory, but the Committee do not explain how this contaminated zinc is to be prepared. Stirring the pure melted zinc with iron wire gives sufficient iron to it to render it useless for delicate arsenic tests, but the addition of one-and-a-half parts of metallic iron melted with 2000 parts of pure zinc might be employed. I have tried adding minute quantities of different metals to pure metallic zinc. Nickel answers the purpose best, as the smallest quantity of that metal produces the greatest effervescence, but on the whole I prefer the use of a solution of sulphate of copper, as the most constant mirrors are obtained by this method.

Chloride of Calcium.—The Committee suggest that this substance, used in the drying tube, often contains arsenic, which should be separated. They do not say that such

arsenic has been found to act injuriously on the test. I was told that molecular hydrogen was capable of removing arsenic from solutions, and tried the experiment, but my results showed that this was not the case.

Apparatus.—A 200 c.c. flask is recommended by the Committee in which to make the Marsh-Berzelius test. I have found that size of flask to be too large, and I use a flask of 50 c.c. capacity. The fitting of drying tube with cotton-wool and chloride of calcium I agree with, and also the use of the roll of dry blotting-paper containing acetate of lead. I prefer, however, to put this roll in the front end of the tube used for obtaining the mirror, and I do not see the use of the bulb at the end of the drawn-out portion, as shown in the Committee's diagram of this tube—but this is an unimportant detail. By my method I soften by the blowpipe and draw out a piece of tube 200 m.m. long, $4\frac{1}{2}$ m.m. internal, and $6\frac{1}{2}$ m.m. external, diameter, from the middle, thus producing two tubes, each of 100 m.m. long, with 140 m.m. of drawn-out portion between them. The drawn-out portion is cut in the middle, leaving two tubes with 70 m.m. drawn out from each; the drawn-out portion for receiving the mirror being about 2 m.m. internal diameter.

At 70 m.m. from the drawn-out end the glass is again softened and drawn out for 30 m.m., and in the remaining 30 m.m. portion of the tube at the end is inserted a roll of filter-paper previously soaked in a strong solution of lead acetate and dried. I do not regard the passage of the gas through a solution of acetate of lead as satisfactory, as some of the arseniuretted hydrogen is dissolved and retained by the solution.

When the test has been completed the point of the drawn-out portion is sealed, and the drawn-out portion at the other end is also sealed by the blowpipe. I have examined mirrors which have been thus sealed in hydrogen in comparison with others left unsealed, and have not been able to observe any difference between them after many months. But I am not prepared to say that the mirrors may not fade by exposure to light and air, and under any condition I think it is desirable to seal up the tube and preserve the mirrors in an atmosphere of hydrogen.

I think the arrangement devised by me for introducing the solution to be tested is an improvement on the arrangement with the glass tap suggested by the Joint Committee. In this I grind the end of a glass rod into the end of the thistle tube entering the Marsh-Berzelius flask, which has previously been rounded in slightly, by softening the end in a Bunsen flame; on raising the rod the liquid flows in, and on letting it down the flow stops. By this means no column of liquid is left in the tube, as is the case when a glass tap is used, and no gas can rise through this simple stopper.

The Joint Committee think rather denser mirrors are obtained with minute quantities of arsenic when using hydrochloric acid than when using sulphuric. I have devoted some attention to this, but have not been able to get such results. I think it is possible that hydrochloric acid, which cannot usually be obtained quite free from arsenic by the Joint Committee's method, may account for this difference. At all events I have not been able to find any appreciable difference in the mirrors obtained for the same quantity of arsenic when working with hydrochloric and with sulphuric acids respectively.

The Joint Committee's suggestions as to testing beer, yeast, &c., directly and without destroying the organic matters do not seem satisfactory to me. No mirror is shown unless the article contain comparatively large quantities of arsenic, and this can only be regarded as a very rough test.

My experiments show that the direct testing of beers containing less than $\frac{1}{100}$ th of a grain of arsenic trioxide per gallon is utterly untrustworthy. In some cases beers containing that quantity give a slight yellow mirror, and in some cases with $\frac{1}{100}$ th they give no mirror, whilst this amount is easily detected and estimated after the organic matter is destroyed.

Destruction of the Organic Matter.—The old process suggested by the Joint Committee for this purpose seems to me clumsy, and involves more work and attention than the one used by me. The Joint Committee's process involves treatment by nitric acid and afterwards charring the organic matter with sulphuric acid, the charred mass being then washed with water and the washings concentrated. Tests carried out with this process in comparison with my own, in which all the organic matter is removed by oxidation, showed that the former process takes a longer time and gives considerably smaller arsenic mirrors than the latter. I found the direct electrolytic method, although generating arseniuretted hydrogen when the arsenic is present in considerable quantities, was quite useless for detecting minute quantities of arsenic.

I understand that the Joint Committee's processes were tested by other members of the Committee on samples containing known quantities of arsenic. It is unfortunate that the results obtained by the different members of the Committee have not been published.

The following is the process which I have found to be most satisfactory for approximately determining small quantities of arsenic in beer, malt, &c.

Process for Estimation of Arsenic in Beer and Stout, Malt, Caramel, &c.

Beer.—Take of the sample 50 c.c. and evaporate to a syrup on a sand-bath or iron plate in a 200 c.c. Jena glass flask. Add 25 c.c. strong nitric acid and 5 c.c. strong sulphuric acid; place on a hot sand-bath, having taken away the flame; allow the first violent action to subside, the acid fumes from which may be drawn away through a glass tube in the mouth of the flask by a water Sprengel pump through a solution of caustic soda in a Wolff's bottle. Then apply a Bunsen flame to the sand-bath, and evaporate till the liquid begins to darken. When this occurs add strong nitric acid in quantities of 3 c.c. at a time (the total quantity of nitric acid required varies from 30 to 50 c.c., depending on the quantities of organic matter present), until on further heating it continues colourless, and fumes strongly of sulphuric acid; cool, dilute with 10 c.c. of water, and boil down to break up the nitro-sulphuric acid formed. When cold, dilute with 10 c.c. of water, and deliver into the Marsh-Berzelius apparatus, the capacity of which should not exceed 50 c.c. The gas evolved should be dried over calcium chloride contained in one tube 70 m.m. long by 8 m.m. diameter.

Testing Reagents.—A blank on the reagents and apparatus used should be made by boiling down 100 c.c. HNO_3 and 5 c.c. H_2SO_4 till all nitric is expelled, diluting and boiling down (this procedure removes every trace of nitric or nitrous acid), again diluting, and testing in the Marsh-Berzelius apparatus as above described.

Process for Malt, Sugar, Caramel, Hops, Yeast, &c.—Take 5 grms. of malt or other solid organic substance, add 25 c.c. HNO_3 , and heat gently till the first violent action is over; then add 5 c.c. sulphuric acid, and proceed as for beer (a total of from 50 to 75 c.c. of nitric acid will be required).

The Marsh-Berzelius Apparatus (50 c.c. flask) should contain about 20–25 grms. zinc. The CaCl_2 in the drying tube should be renewed as soon as the first few pieces become wet.

Action is started by adding 5 c.c. of dilute sulphuric acid (10 parts concentrated sulphuric, 20 of water, and 1 part of a 10 per cent solution of pure crystallised copper sulphate). Allow the evolution of gas to go on (the exit tube for the hydrogen being heated in the usual manner by means of a small Bunsen flame) until the hydrogen nearly ceases to be evolved (I see no advantage in removing the air from the apparatus by means of hydrogen generated in another apparatus); then fill up the tube and funnel of the Marsh-Berzelius apparatus with the solution previously treated as above, and allow the whole to run

in if only a very minute quantity of arsenic is supposed to be present; or run in an aliquot part if a larger quantity is supposed to exist. In about fifteen minutes the flask is washed with 5 c.c. more of the above acid, which is added to the hydrogen flask in small quantities at a time to keep up the evolution of gas for a total of from thirty to thirty-five minutes after the first introduction of the previously treated beer, by which time, with this sized apparatus, all the arsenic will have passed off.

The hydrogen flame at the end of the drawn-out portion should be about 2 m.m. long, and maintained as constant as possible; too slow a flow almost invariably gives double mirrors, too fast a flow gives irregular ones difficult to compare with the standards.

Zinc.—Twenty grms. of zinc should be tested by the action of 30 c.c. of dilute H_2SO_4 —one of acid to two of water—containing a little copper sulphate to start the reaction as above described; there should be absolutely no trace of arsenic mirror on the drawn-out portion of the glass tube.

Another experiment should then be made, adding a minute quantity of arsenic, say equal to $1/5000$ of a grain per gallon (when working on 50 c.c.), equal to 0.029 part per 1,000,000, or an actual weight of 0.00143 m.grm., and compared with a standard tube to make sure that the zinc contains nothing which will hold back minute quantities of arsenic.

Glass tube should be about $4\frac{1}{2}$ m.m. internal diameter, and about 6 $\frac{1}{2}$ m.m. external. It should be drawn out in the middle and at the end, the length of the drawn-out portions respectively being 30 m.m. and 70 m.m., and the portion of tube between the drawn-out portion being 60 m.m. The diameter at the beginning of the drawn-out portion for receiving the mirror is about 2 m.m. internal diameter.

A piece of fine iron gauze 20 m.m. wide is wrapped round the tube at the point A shown in the figure, and heated by a Bunsen flame. This is a more satisfactory plan than applying the flame directly to the tube, and conduces to the formation of more uniform mirrors.

A roll of lead acetate paper is introduced to absorb any traces of sulphuretted hydrogen which may be formed.

Bunsen Flame.—This should be about 4 in. long, and protected till near the point by a conical iron or copper chimney of about 2 $\frac{1}{2}$ in. high by 2 $\frac{1}{2}$ in. at the lower, and 1 $\frac{1}{2}$ in. diameter at the higher part of the cone c.

Heating the Tube.—This should be heated from the shoulder, or drawn-out portion, for about $\frac{1}{2}$ in. at the point A.

Standard Mirrors for comparison are made by introducing into the apparatus known quantities of arsenic, say, commencing with $1/500$ of a grain per gallon when working on 50 c.c. A convenient method of preparing the standard mirrors is to employ a solution of arsenious acid containing 0.007145 of a m.grm. of As_2O_3 per 1 c.c. One c.c. of this solution is equal to $1/1000$ of a grain of As_2O_3 per gallon when using 50 c.c., or $1/1000$ of a grain per lb. when using 5 grms. of material. This solution is suitable for standards between $1/500$ and $1/1000$ of a grain per gallon, and a solution of one-tenth this strength may be employed for the standard mirrors between $1/1000$ and $1/10000$ of a grain per gallon.

The mirrors I have found most useful are $1/500$ th, $1/666$ th, $1/888$ th, and $1/1000$ th of a grain per gallon, corresponding to 2.0, 1.5, 1.25, and 1.0 c.c. of the stronger solution, and $1/1111$ th, $1/125$ th, $1/143$ rd, $1/166$ th, $1/200$ th, $1/250$ th, $1/333$ rd, $1/500$ th, $1/666$ th, and $1/1000$ th of a grain per gallon, corresponding to 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.5, and 1.0 c.c. respectively of the weaker solution.

The second figure gives photographic representations of different amounts of arsenic deposits from beer. The figures on the tubes show fractions of a grain per gallon, using 50 c.c. of beer in each test.

Cacodylic Acid.

I have made experiments with a view of finding whether

the arsenic contained in this compound could be estimated by my process:—

1. I added directly cacodylic acid representing $1/1000$ th of a grain of As_2O_3 to the Marsh-Berzelius apparatus. This would have given a very heavy mirror if the arsenic had been eliminated as arseniuretted hydrogen; but an arsenic mirror was formed equivalent to about one-tenth of the quantity taken, which was probably not due to the arsenic in the cacodylic acid.
2. Cacodylic acid, equivalent to $1/10000$ th of a grain of As_2O_3 was digested with nitric and sulphuric acids in the ordinary way, and also with fuming nitric acid, heated under pressure in a hermetically sealed glass tube, the nitric acid being then removed in each case, and the solution "marshed," but no arsenic from the cacodylic acid was indicated in either case.
3. Fifty c.c. of the solution containing cacodylic acid equivalent to $1/1000$ th of a grain of As_2O_3 per gallon were treated with nitric and sulphuric acids in the ordinary way, along with potassium permanganate (which was suggested by Villiers for breaking up organic compounds), by using 10 c.c. of a half per cent solution of potassium permanganate in addition to the sulphuric and nitric acids; the cacodylic acid was thus destroyed, and its equivalent arsenic mirror was obtained.

NOTE ON THE ESTIMATION OF SODIUM CHLORIDE IN SOAPS.

By A. R. WARNES.

SOME discordant results having been obtained when examining a bar of soap for sodium chloride, the following experiment was carried out to prove the accuracy of the method used:—

A sample of soap was made in the laboratory, using chlorine-free materials. Ten grms. of this pure soap were taken and dissolved in water in a 6-oz. beaker. To the solution a known quantity of pure sodium chloride was added, the fatty acids then thrown up with sulphuric acid, and the beaker and contents heated on the water-bath until the aqueous layer became clear. The beaker was allowed to cool, then the cake of fatty acids was pierced in two places and the aqueous layer poured into a separating funnel. The fatty acids and the interior of the beaker were then well washed with cold water, and the washings added to the liquor in the funnel. Petroleum ethers (all over under 80° C.) were added, and the funnel well shaken in order to extract traces of dissolved fat acid. After separation, the aqueous layer was run into an 8-oz. conical flask, one drop of phenolphthalein indicator added, and ammonium hydrate added until solution became just pink. The flask was then placed on the water-bath and left until any retained petroleum ether was driven off, and then boiled until the vapours showed no reaction with red litmus-paper. The liquor was then cooled and titrated in the usual way with $N/10$ $AgNO_3$. Afterwards a little nitric acid and excess of silver nitrate were added, and the sodium chloride determined gravimetrically.

The results of two experiments are tabulated below.

	NaCl added. Grm.	NaCl found volumetrically. Grm.	NaCl found gravimetrically. Grm.
1.	0.0423	0.0427	0.0422
2.	0.030	0.0307	—

Differences of Potential Contact.—Pierre Boley.—The author examines the action of piles formed of amalgams of the metals ordinarily used with sulphuric acid. He finds that the differences of potential between the amalgams is so small as to be only a few millivolts—values which are of the same order as the possible errors of the experiment.—*Comptes Rendus*, cxxxv., No. 11.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

THE General Monthly Meeting of the Society was held at the Society's House, No. 5, Elizabeth Street North, on Wednesday evening, July 2, 1902; Prof. WARREN, M.Inst.C.E., Wh.Sc., President, in the Chair.

The following paper was read:—

"Notes on Two Chemical Constituents from the *Eucalypts*." By HENRY G. SMITH, F.C.S., Assistant Curator, Technological Museum.

In this paper the author records the results of continued investigations on the ester (geranyl-acetate) contained in the oil of *Eucalyptus Macarthurii*, and also on the oil itself. This data shows that the ester does not fall, at any time of the year, below 60 per cent, and that the amount of free alcohol, considered as geraniol, diminishes in amount as the ester increases. The greatest amount of naturally formed ester occurring at any time of the year was 74.9 per cent in September, but the free alcohol was only 6 per cent at that time. It has been found from numerous determinations that when the oil is acetylated the ester content will be but little removed from 80 per cent. The oil does not contain phellandrene at any time of the year, and eucalyptol appears to be always absent. Eudesmol is always present, but as it varies in amount, the specific gravity of the oil varies also. The crude oil appears to be always slightly dextro-rotatory. From the results of investigation of the oil obtained from over 200 distinct species of *Eucalypts*, this is the only one found to contain this valuable oil. The author also shows that the original formula for the quercetin glucoside, myrticolorin ($C_{27}H_{28}O_{16}$), obtained from the leaves of *Eucalyptus macrorhyncha* was correct (*Trans. Chem. Soc.*, 1898, p. 697). This formula has been confirmed by Mr. A. G. Perkin, who has shown (*Trans. Chem. Soc.*, 1902, p. 477) that his own osyritrin, and also Mandelin's violaquercitrin have the same formula, and are identical substances with myrticolorin. They all form quercetin and glucose on hydrolysis.

The following is an abstract of the first Science Lecture of the present Session, delivered on June 30 by F. TIDSWELL, M.B., M.Ch., D.P.H., Health Department, on "The rôle of Bacteria in the Production of Disease."

The lecture opened with an account of the discovery of bacteria over two centuries ago by the Dutchman Anton van Leeuwenhoek. Allusion was then made to the subsequent controversies concerning the origin of bacteria, and their influence in causing disease, and the manner in which their final settlement was effected by the researches of Louis Pasteur some thirty years ago. Attention was then directed to Pasteur's demonstration of the causal micro-organism of a disease affecting silkworms, and of Davaine's observations on the microbe of anthrax. It was shown how these results stimulated investigation of the germ theory, and how the proof of its correctness was rendered possible by the elaboration of exact bacteriological methods by Robert Koch. Mention was then made of the species of bacteria which produce disease in man. There followed a brief account of the structure and functions of bacteria in general, and the specialisation of some forms into producers of disease. The consideration of the occurrence of these bacteria in the surroundings of the sick, and even upon the healthy skin, led up to an account of Lister's institution of methods for preventing their entry into wounds, and its development into the modern system of aseptic surgery and of the principles underlying the hospital isolation of the infectious sick, and disinfection. The means by which infectious bacteria gain access to the surface of the body, and the events connected with their entrance to, and development in, the internal tissues were dealt with at length. It was pointed out that the manifestations of these diseases depend upon the injury done to the tissues by the poisons or toxins produced by the

bacteria, and that recovery from them is consequent on the elaboration of neutralising substances or antitoxins by the cells of the body. Reference was then made to the after-effects of these diseases, including the immunity against subsequent attacks, and in this connection attention was called to the use of viruses, vaccines, any prophylactics as preventives, and of antitoxic serums as cures for infectious diseases.

OBITUARY.

JOHN HALL GLADSTONE, PH.D., F.R.S.

It is with great regret that we announce the death of Dr. John Hall Gladstone, which has just occurred suddenly and unexpectedly on Monday morning last, the 9th inst.

Dr. Gladstone was born on March 7th, 1827, and was therefore in his seventy-sixth year. He first studied chemistry at University College, London, under Prof. Graham, then at Giessen under Prof. Liebig. He took the degree of Ph.D. in 1848, and was elected a Fellow of the Royal Society in 1853; he was the first President of the Physical Society on its foundation in 1874, and was President of the Chemical Society from 1877 to 1879.

Dr. Gladstone's first paper was published in the year 1845; it was entitled "Contributions to the Chemical History of Gun-cotton and Xyloidine." Since that time he has been constantly engaged in scientific research, principally in chemistry and optics, and the points of contact between these two sciences. In conjunction with the late Dr. Alfred Tribe, he published a large number of papers on chemical activity with regard to electrolysis, the copper-zinc couple, &c.

Dr. Gladstone may be said to have died "in harness," as his last paper, "On Fluorescent and Phosphorescent Diamonds," and one in conjunction with Mr. W. Hibbert, "Colloids of Zirconium, compared with those of other Metals of the Fourth Group," were only quite recently read at the meeting of the British Association at Belfast, and appear in this number of the CHEMICAL NEWS.

But it was not only in scientific circles that Dr. Gladstone was well known; for many years he had been engaged in various philanthropic and religious movements, and from 1873 until 1894 he represented Chelsea on the London School Board, of which he was also Vice-Chairman.

Amongst other books of which he was the author, we may mention "The Biography of Michael Faraday," "Spelling Reform from an Educational Point of View," and the "Chemistry of Secondary Batteries."

In private life his pleasant face and genial manners have endeared him to a large circle of friends. He was also a well-known and constant attendant at many scientific meetings, where his kindly presence will be greatly missed.

PROFESSOR JOHN JAMES HUMMEL, F.I.C.

In the death of Professor Hummel, F.I.C., the dyeing world has lost one of its most brilliant exponents. He was the pioneer teacher of this subject, an arduous worker, and scientific investigator. The experience acquired in the works as manager, and also as practical chemist, combined with his training in the Technical School at Zürich under Stadeler and Wislicenus, qualified him for the work of initiation in the Dyeing Department of the Yorkshire College, with which his name will always be associated.

John James Hummel was of Lancashire birth, being born in Clitheroe, but his father was a native of Switzerland, and a technical chemist, occupying positions of responsibility in Dyeing and Printing works at Elbeuf, Paris,

and Rouen, and subsequently chemist in the printing works of James Thomson, F.R.S., of Clitheroe. The influence of Mr. Thomson brought him into touch with many eminent scientific men, among them being Frederick Steiner, John Mercer, Walter Crum, Daniel and Camille Koechlin. It was only natural that Mr. Hummel should inherit ability for scientific pursuits, and that, though for a time he entered business, he should manifest decided taste for some branch of technical chemistry.

After his training under Mr. G. Knecht, B.Sc., and a short term in a Manchester office, he was three years in the Polytechnic School of Zürich, where he obtained his diploma, and adopted the profession of his father, entering a calico print works as chemical adviser. Dr. Crace Calvert, F.R.S., offered him an assistantship in the Manchester Royal Institution Laboratory, but this he declined, accepting the post of chemist in the print works of Messrs. James Black and Co., near Glasgow. His faculty for teaching, and interest in, technical education were first exercised whilst with this firm, for he formed a class in chemical technology, bearing specially upon dyeing and printing, imparting instruction gratuitously, and not a few of the young men attending attribute their success in life to this training. Later, he was manager in a print works in Lancashire, and for a firm of woollen-yarn dyers in Scotland.

In 1879, the Clothworkers' Company of the City of London extended their departments at the Yorkshire College by establishing a school of dyeing, and Mr. Hummel, early in 1880, was appointed the head of the new department. His success as a teacher was soon recognised, and in 1885 well-equipped buildings with suitable lecture-room, museum, experimental dye-house, and laboratories were erected. Since that time, students have been trained under Professor Hummel from all parts of the United Kingdom, the Continent, America, Canada, Japan, and other countries.

Some four years ago Professor Hummel advocated the importance of scientific research in the chemistry of dyeing, and as a result the research laboratory and other extensions of the dyeing department were equipped and formally opened in May, 1900. These also comprise pattern and practical dye-houses, so that the equipment which Professor Hummel designed and carried out with a mastery of detail is such as to be superior to that of any other school of dyeing in the world, and to effect the teaching of dyeing in the fullest degree, both in its pure scientific and practical phases.

The commencement of this work, and of the woollen and worsted yarn-spinning branches of the textile industries department, have produced an educational unity between the Clothworkers' departments which has made it feasible to teach the science and practice of the manufacturing of all kinds of woollen, worsted, and mixed fabrics, not yet possible to the same extent in any Continental or American school. The experiments conducted are of such a nature as to show the influence of the dyeing processes upon the nature of the material, the spun yarn, and the woven fabric. Many fields of research are, between the departments, being investigated. The able manner in which the dyeing extensions have been designed, and the work sub-divided into pure scientific research, experimental dyeing, and pattern and practical dyeing, have made the course of study increasingly valuable. So far as the practical dyeing of materials, yarns, and cloth was concerned, the desire of Professor Hummel was to perform it with the same method and business accuracy as characteristic of actual works.

As a lecturer and teacher of experimental science the late Professor possessed natural and trained ability. Fluent and clear, and competent of expounding every detail of the subject dealt with, his style was methodical, analytical, and concise. In his lectures he had recourse to his experience in the works, and, recognising the value of illustration and experiment, he made ample use of diagrams, lantern-slides, and specimens. Those who

have studied under him have many incidents by which to recall his kindness, willingness to help in a difficulty, and to render to the earnest seekers after knowledge the best of all assistance, sympathetic encouragement.

Mr. Hummel has made several valuable contributions to literature on the science and technology of dyeing. His principal work, "The Dyeing of Textile Fabrics," has been translated into German, Italian, and Japanese, and his articles on dyeing in the "Encyclopædia Britannica" and in various scientific and technical journals, are well known to the dyeing industry. In recent years his energies had been so absorbed with the new buildings that his literary activities had to be curtailed, but I have reason to believe that he was gleaning information and making experimental research which would have ultimately been published.

None who knew Mr. Hummel intimately can readily forget his uniform thoughtfulness, true sympathy, and friendship. He was in every sense devoted to the task with which his life was so fully associated, but this did not prevent him manifesting enthusiasm in the solution of the difficulties of others. He was highly esteemed by his colleagues, by the Textile and Dyeing Committees, and the Clothworkers' Company. A sincere and true man, he was faithful to duty, and lived for the high purpose of extending scientific knowledge and for the exercise of influences which would better humanity. In the dyeing department of the Yorkshire College, which his endeavour has organised, there is a memorial of industry and of lasting service rendered to the science and art of dyeing.

NOTICES OF BOOKS.

Thirty-eighth Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. London: Eyre and Spottiswoode.

THIS report, presented to the Local Government Board under the Alkali, &c., Works Regulation Act, summarises the state of chemical industry in the United Kingdom during the year 1901. Compared with 1899 and 1900, the Inspector has to record a reduction on the whole, both in the number of works and of processes. The report includes a valuable paper by Dr. Affleck on "The Composition of Gases Evolved in the Manufacture of Superphosphate Manures, and a more Accurate Method of Determining their SO_3 Equivalents," which will be read with much interest by all chemists; and also the results of further experiments, carried out in the Chief Inspector's own laboratory, on the action of ferrous thiosulphate on sulphuretted hydrogen; the methods employed being closely allied to those described in last year's report.

Wireless Telegraphy. By G. W. DE TUNZELMANN, B.Sc. Third Edition. London: The Office of Knowledge. 1902.

THIS "Popular Exposition" is based upon a series of papers on wireless telegraphy which appeared in *Knowledge* during the year 1900, but a good deal of matter has been added to bring them up to date. The book is intended primarily for the general reader who is practically ignorant of physics. Regarding it from this point of view, we are inclined to think that such a reader might well have been supposed to possess more knowledge of the elements of mathematics, though perhaps it would be difficult to set a limit to the introduction of formulæ if once begun. There is sometimes a great want of cohesion in the treatment of the subject, and some paragraphs will undoubtedly have to be re-read to discover the author's meaning. Many of the illustrations are borrowed from Lodge's "Modern Views of Electricity" and the *Electrical Review*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 11, September 15, 1902.

Electric Resistance of Badly-conducting Bodies at very Low Temperatures.—Edmond van Aubel.—The electric resistance of metals and alloys at very low temperatures has been measured by Dewar and Fleming and by Arsonval. It is found to diminish considerably in proportion as absolute zero is approached. The author now examines the electric resistance of badly-conducting bodies, such as certain oxides and sulphides, whose electric conductivity increases during the elevation of temperature from 0° to 100°. The first experiments were carried out on a very homogeneous specimen of pyrites, FeS_2 , and it was found that the resistance of the pyrites increased as the temperature was reduced, but it still conducts to a certain extent even, in liquid air. The author is now continuing his researches on other sulphides.

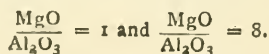
Formation of Liquid Drops and Tate's Law.—Ph. A. Guye and F. Louis Perrot.—The authors find that, under ordinary experimental conditions, the weight of drops issuing from the same orifice and rapidly formed is greater than that of those formed slowly; also, if the duration of formation increases, the weight of the drop tends towards a limit, which practically does not vary if the time of formation is long enough. With a tube of 3.17 m.m. of exterior diameter, the weight of the drop is independent of the time of formation only if this is thirty to forty seconds, or, for certain liquids, even from twenty to twenty-five seconds.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 5.

Ammonio-calcic Phosphate.—Henri Lasne.—Already inserted in full.

Action of Oxide of Bismuth on various Metallic Solutions.—J. Aloy.—On boiling recently precipitated oxide of bismuth for one hour with saline solutions, the author has observed that with ferric salts the Fe is only completely displaced in weak solutions. With ferrous salts the Bi displaces the Fe from the chloride, even in the cold, but much more easily when boiled; it forms a greenish white precipitate, easily oxidised, consisting of a mixture of basic salts, or perhaps of a mixed basic salt; the amorphous form of the precipitate renders it impossible to decide between these two hypotheses. As with iron, aluminium is only completely displaced in very dilute solutions. With manganese the displacement is partial. Copper is partially displaced from its concentrated solutions of the chloride, nitrate, and sulphate, in the form of greenish blue basic salts; in the case of the acetate the black hydrate is precipitated. The metals cobalt, nickel, lead, zinc, and cadmium also are partially displaced from their solutions. The anhydrous oxide produces the same reactions, but much less readily than the precipitated oxide.

An Electric Heating Apparatus.—M. Guntz.—Instead of using a fine platinum wire embedded in asbestos or enamel for the purpose of obtaining high temperatures of 1200° to 1300°, the author used a brasque of aluminate of magnesia or lime for covering the wire, and found that it protected the wire from all alteration. This method has the great advantage that apparatus of any form can be heated; muffles and furnaces of any desired shape can be constructed very quickly, and if desired the heat can be distributed unequally by increasing or decreasing the spaces between the spirals, or the section of the wires. The brasque of aluminate of magnesia was made of two mixtures:—



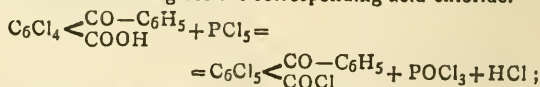
The calcined alumina and magnesia are finely pulverised and passed through a silk sieve. The paste is made with a little water and gelatinous alumina, which causes it to be slightly plastic; a dilute solution of acetate of alumina can also be used. The brasque of aluminate of lime is easier to make; it is formed by mixing 1 part of strongly calcined Al_2O_3 , 1 part of Al_2O_3 produced by the incomplete calcination of ammonia-alum, and 1 part of aluminate of lime obtained by heating equal weights of pure lime and alumina to redness. Care must be taken that no sensible amount of silica is present.

No. 6.

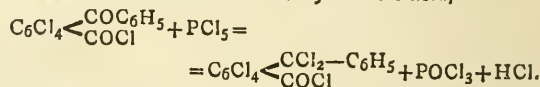
Action of Hydrates of Copper on Aqueous Solutions of Metallic Salts.—A. Mailhe.—Already noticed.

Action of Binoxide of Sodium on the Metals of the Platinum Group.—MM. Leidie and Quennessen.—Already noticed.

Action of Pentachloride of Phosphorus on Tetrachloro-*o*-benzoylbenzoic Acid.—L. Tétrý.—The action of pentachloride of phosphorus on tetrachloro-*o*-benzoylbenzoic acid first gives the corresponding acid chloride:—



but the pentachloride of phosphorus, under the conditions of the experiment, reacts on the latter, giving the tetrachlorised chloride of dichlorobenzylbenzoic acid,—



Direct Analysis of Essence of Pennyroyal.—L. Tétrý.—Essence of pennyroyal was submitted to fractional distillation *in vacuo* under a pressure of 20 m.m., and three portions were obtained; the principal portion, boiling at 110–112°, consisted of the raw pulegone. The author describes two methods for the examination of this product. The first consists of transforming the menthol into benzoate, easily separated from the pulegone by distillation *in vacuo*. The second method consists of transforming the pulegone, and the ketones which may accompany it, into oximes, of which the boiling-points are naturally much higher. These oximes are separated by distillation *in vacuo*, and the menthol looked for in the most volatile portion. The other portions of the essence of pennyroyal were submitted to fractional distillation *in vacuo*; a considerable quantity was obtained boiling at 60–90° under 20 m.m., and another passing over at 90–110° at the same pressure.

Action of the Alcoylcyanacetic Ethers on the Diazoic Chlorides.—M. Favrel.—Already noticed.

Action of the Acidylcyanacetic Ethers on the Diazoic and Tetrazoic Chlorides.—M. Favrel.—Already noticed.

Chemical Modifications in Plants submitted to the influence of Chloride of Sodium.—E. Charabot and A. Hébert.—Already noticed.

TO PHYSICISTS, ELECTRICAL ENGINEERS, &c.

An Established Firm of Scientific Instrument

Makers of some repute, with a steadily increasing clientele, are desirous of meeting with a Gentleman possessing a Scientific Training and an aptitude for commercial life as PARTNER. One in possession of a University Degree and a moderate amount of capital would find an exceptional opportunity for speedy advancement. The Business is well established and the present proprietors are well known in Scientific Centres. The matter will bear the strictest investigation and is capable of almost unlimited increase. The Works are equipped with Modern Appliances and a staff of well trained workpeople. The firm has a reputation for Modernised and Moderately-priced Apparatus—in contradistinction to the cheap, useless rubbish now so largely sold. They also possess several Specialities of their own, the increasing sale of which is proof of their utility among Science Teachers and Educational centres.—Principals or their Solicitors are invited to reply to "Physics," CHEMICAL NEWS Office, 6 & 7, Creed Lane, Ludgate Hill, London, E.C.

Co ..	59	72
Pd ..	106	0.43
Pt ..	194	0.88

All, except the terminal members in some of the groups, show an inverse relation of atomic weight to relative distribution. In the case of the halogens, it is possible to get an approximation to their *absolute* distribution. Such an estimation is based on the following considerations:—Haloid compounds are admitted by geologists to have been amongst the last to form or condense on the earth's surface. Solvent denudation for untold ages has effectually carried them to the sea, which has been their great receptacle, and it is a reasonable assumption that what is left on the land is a negligible quantity when compared with the vast mass existing in the sea. On this subject wrong ideas are prevalent, based principally on river analyses. It is only necessary for me to point out that the annual fluvial load of haloid compounds is mainly circulatory, and that the portion derived *de novo* from the earth is probably not more than 8000 millionths of what is already in the ocean (Ackroyd, *CHEMICAL NEWS*, lxxxiii., 268; *Geol. Mag.*, October, 1901, p. 448; and *Proc. Yorks. Geol. and Polytechnic Society*, xiv., 411). Given, then:—(1) The ratio of chlorine to bromine and of chlorine to iodine in the sea, and (2) the mass of its chlorine contents, one may compute what is their respective per cent of the earth's mass. Adopting the most recent data for all weights and measurements concerned, I get the following figures:—

R.	Atomic weight.	Relative distribution in per cent of the earth's mass.
Chlorine	35.5	0.000486
Bromine	80	0.00000583
Iodine	127	0.000000583

Or we may express the results as follows:—

a.	b.	c.	$\frac{c}{b}$
R.	Atomic weight.	Per cent of earth's mass.	Atomic distribution.
Cl..	35.5	4.86×10^{-4}	0.136×10^{-4}
Br .	80	5.83×10^{-6}	0.0728×10^{-6}
I ..	127	5.83×10^{-8}	0.0459×10^{-8}

An inverse relation of distribution to atomic mass is strikingly apparent.

The exceptions to this rule occur at the two extremes—among the lightest non-metals and the heaviest metals. As such a law will probably embrace all the elements in the universe, and certainly not less than exist in the solar system, it is within the bounds of probability that the lighter non-metallic elements, absent in requisite proportions in the earth, may exist to a preponderating extent in the outer planets and be a cause of their marked lesser density. This view has already been advocated by Sir J. N. Lockyer, on other grounds entirely, in the course of his Manchester lectures in 1876 ("Science Lectures for the People," Eighth Series, p. 160, John Heywood).

The anomalous position of some of the metals of highest atomic mass is illustrated by the case of barium. This element is more plentiful than its immediate predecessor, strontium—a peculiarity also possessed by mercury, lead, thallium, osmium, platinum, iridium, and thorium. If, however, the distribution figures be divided by the respective atomic weights, mercury, barium, osmium, and iridium cease to be anomalous; platinum is only just over the dividing line, while lead, thallium, and thorium still remain exceptions which might perhaps conform to rule if one could only become possessed of their absolute distribution figures.

In addressing this Section in 1886, Sir William Crookes conjured up the beginnings of things before the earth was thrown off from the central nucleus—a primal stage of ultra-gaseous matter, a vast sea of incandescent mist—when the atoms could not yet have been formed. In time, by some process akin to cooling, this primordial matter (protyle) formed itself into atoms. Does it not now appear that during this genesis of the elements—this transmutation of protyle into complex elemental forms—less and less atoms of highest mass were evolved, and that the

universe became pervaded by the greatest quantity of those atoms which have the lowest masses?

APPENDIX.

Ratio of the Halogens in the Sea.—The extreme values for Cl:Br are 100:0.32 from C. J. S. Makin's "Analysis of the Atlantic" (*CHEMICAL NEWS*, lxxvii., 155), confirming Dittmar's *Challenger* results, and 100:2.11 from Usiglio's figures for the Mediterranean ("Watts's Dictionary," v., 1017). The mean Cl:Br is 100:1.2. Gautier found 2.4 mgrms. of I per litre in sea-water (*Comptes Rendus*, 1899, cxxviii., 1069). Taking the Cl to be roundly 20,000 mgrms. per litre, we obtain the ratio Cl:I = 100:0.012, which is nearly identical with the ratio obtained from Sonstadt's earlier data (*CHEMICAL NEWS*, xxv., 196, 231, 241).

Earth's Mass.—The mean density is taken as 5.472, the average of eight determinations by Maskelyne, Cavendish, Reich, Baily, Airy, James, Poynting, and Plana and Carlini; and the mean diameter as 7912.4 miles, which gives a mass of 5812.4×10^{18} tons.

Mass of Chlorine in the Ocean.— 28286×10^{12} tons.

THE COLOUR OF IODINE-CONTAINING COMPOUNDS.*

By Miss IDA SMEDLEY.

PROFESSOR H. E. ARMSTRONG (*Proc. Chem. Soc.*, 1892) has for some years contended that a generalisation may be made as to the molecular structure of substances which are visibly coloured in the conventional acceptance of the term, since almost all coloured organic substances may be represented by a "quinonoid" structure, if the term "quinonoid" be regarded as including any compound, which contains at least three centres, having some influence on the passage of light through the molecule. From this point of view he regards iodoform as a quinonoid substance in which the three iodine atoms act as centres co-operating to produce colour.

Substances containing iodine may be divided into two classes—coloured and colourless. Does any distinctive similarity of structure exist in the coloured iodine-containing compounds?

Of the molecular condition of solid iodine nothing is known; in solutions the number of atoms in the molecule probably lies between two and four (Loeb, *Trans. Chem. Soc.*, 1888). The violet vapour up to 700° C. consists of di-atomic molecules; but completely dissociated or gaseous mon-atomic iodine is described as colourless. The iodine halogen compounds are also coloured, the mono-chloride much more intensely than the tri-chloride. When iodine acts as a trivalent element, combination with one chlorine atom is insufficient to produce colour: thus di-phenyl iodonium chloride (IPh_2Cl) is colourless, but phenyl iodide chloride (IPhCl_2) is yellow.

Since the iodine atom itself is probably colourless, the colour of the compounds must be attributed to the mutual effect of the halogen atoms. Further, a comparison of the iodine chlorides shows that the tendency to produce colour is greater where the iodine atom is not fully saturated.

Amongst the compounds of iodine with other elements, the readiness with which double iodides are formed, the comparative insolubility of many of the iodides, and the colour-changes they undergo on heating, suggest that their molecular structure is more complex than is usually represented. Nearly all the mono and divalent elements give colourless iodides, and it is probable that the coloured di iodides are really polymerised. Mercuric iodide, for instance, which exists in two coloured isomeric forms, gives a colourless vapour, the density of which

* Read before the British Association (Section B), Belfast Meeting, 1902.

corresponds with the simple formula HgI_2 . Among organic substances the exceptional case of di-iodoacetic acid and its salts (Perkin and Duppa, *Annalen*, 185), which are all described as yellow, needs further investigation.

In the case of tri-iodides and higher iodides generally, the appearance of colour is determined, not only by the number of iodine atoms present, but also by the condition of the iodine. Thus the nitrogen group of elements form deeply coloured tri-iodides, while the tri-iodides of boron and aluminium are colourless. In hydrocarbon derivatives the three iodine atoms must be associated with the same carbon atom in order to produce colour, as in iodoform; poly-iodo-derivatives in which the iodine atoms are joined to different carbon atoms, as in tri-iodo-benzene, being colourless.

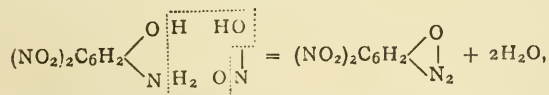
OUR PRESENT KNOWLEDGE OF AROMATIC DIAZO-COMPOUNDS.*

By GILBERT THOMAS MORGAN, D.Sc., F.I.C.

THE aromatic diazo-compounds, which were originally discovered by the classical investigations of Griess (*Annalen*, 1858, cvi., 123; 1860, clxiii., 201; 1866, cxxxvii., 39), have proved to be substances of the utmost value in the development of synthetical chemistry, both from the scientific and the industrial standpoints. The starting-point of these far-reaching researches was a comparative study of asparagine and picramic acid. These substances, which in 1858 were assumed to be compounds of a similar type, behaved quite differently towards nitrous acid, asparagine losing the whole of its nitrogen, whilst picramic acid exchanged three of its hydrogen atoms for one of nitrogen, giving rise to the earliest known diazo-compound—namely, dinitrophenoldiazo-oxide.

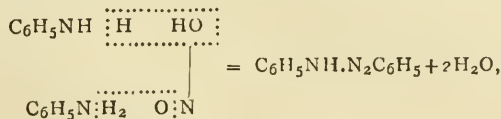
It is interesting to notice at this stage that, although the elimination of aminic nitrogen by the action of nitrous acid is characteristic, not only of asparagine, but also of the majority of aliphatic amino-compounds, yet the preparation of aliphatic diazo-derivatives has been accomplished, and the new field opened up by the discovery of ethyldiazo-acetate (Curtius, *Ber.*, 1883, xvi., 2230) has yielded a rich harvest, culminating in the isolation of hydrazine, hydrazoic acid, and diazo-methane. These important contributions to the chemistry of nitrogen will not, however, be further discussed in this report, which is restricted to a consideration of the aromatic diazo-compounds—a class of substances derived from the hydrocarbons of coal-tar.

The action of nitrous acid on picramic acid is now interpreted in the following manner:—

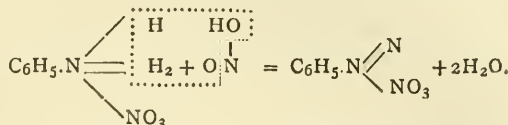


the product being regarded either as the internal salt or the *iso*-anhydride of dinitrophenoldiazo-hydroxide, $(NO_2)_2C_6H_2(OH)N_2OH$ (Hantzsch, *Ber.*, 1896, xxix., 1526).

Griess next extended the investigation to aniline, with the result that diazoaminobenzene was produced,—



and a subsequent modification of the experimental conditions led to the discovery of benzenediazonium nitrate,—



These three substances, the *iso*-anhydride, the diazoamine, and the diazonium salt, each containing a diazo-complex, N_2 , attached to one aromatic nucleus, are typical examples of three important classes of aromatic diazo-compounds.

The process of converting the salt of a primary aromatic amine into the corresponding diazonium derivative is termed diazotisation, and this important operation may be suitably considered under a separate heading.

I. THE PREPARATION AND PRACTICAL APPLICATION OF DIAZO-COMPOUNDS.

A. The Diazo reaction.

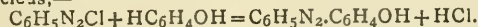
Benzenediazonium nitrate, the substance formed by the action of nitrous fumes on a cold aqueous solution of aniline nitrate, was found to be a highly explosive salt readily soluble in water or alcohol. On account of these properties, the isolation of the salt and the corresponding chloride and sulphate is a somewhat difficult and dangerous operation, and for many years the properties of these substances were studied in the solutions obtained by the action of the alkali nitrites on the primary aromatic base dissolved in excess of cold dilute acid. It has been found by colorimetric and electrolytic determinations of the velocity of this reaction that, in the absence of disturbing influences, all the aromatic amines are diazotised at approximately the same rate (Hantzsch and Schumann, *Ber.*, 1899, xxxii., 1691; 1900, xxxiii., 527).

It is, however, sometimes necessary to operate with the dry diazonium salts, and these may be prepared by the action of amyl nitrite on solutions of the salts of the amines in absolute alcohol (Knoevenagel, *Ber.*, 1890, xxiii., 2094; Bamberger, *Ber.*, 1896, xxix., 446), or glacial acetic acid (Hantzsch, *Ber.*, 1897, xxx., 92; 1901, xxxiv., 3337).

Excess of acid should be avoided in these preparations, for the diazonium chlorides derived from the halogen-substituted anilines combine with hydrogen chloride, forming acid salts of the types RN_2Cl , HCl , and $3RN_2Cl.HCl$ (*Ber.*, 1897, xxx., 1148 and 1153), these products being less stable than the normal salts themselves.

Bamberger showed that pure benzenediazonium chloride, when dissolved in water, gives a neutral reaction, and differs in this respect from aniline hydrochloride, the solution of which is acid, owing to the hydrolytic dissociation of the salt. This result indicates that the strength of the diazonium base is much greater than that of the corresponding primary aromatic amine.

Griess found that the introduction of a diazonium salt into the alkaline solution of a phenol resulted in the formation of an intensely coloured substance containing the diazo-complex, $N:N$, attached to a second aromatic nucleus,—



These products, which are called azo-compounds, are also produced, either by the reduction and coalescence of two molecules of a nitro-compound, or by the condensation of the nitroso-compounds with the primary amines (C. Mills, *Trans.*, 1895, lxvii., 925).

On account of their condensation to form azo-compounds and their ready reduction to hydrazines, the diazonium salts were for many years assumed to have the constitution $R.N:N.Cl$, a formula which was suggested by Kekulé, although Strecker, Erlenmeyer, and Blomstrand had at different times advocated the claims of the symbol—



* Report presented to Section B, British Association, Belfast Meeting, 1902.

According to the former view, which generally prevailed until 1894, the diazonium bases are substances of the oxime type, $RN:NOH$; and this formula, which satisfactorily accounts for the fact, first noticed by Griess, that benzenediazonium hydroxide forms a potassium derivative, is not opposed to the general behaviour of these bases and their salts when employed in the various synthetical operations which engrossed the attention of investigators in this field until the close of the period now under review.

The synthetical application of the diazonium salts will be considered in the next section, since it does not necessarily involve any discussion as to their precise configuration.

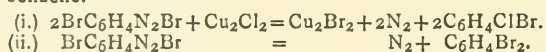
B. Diazo-compounds as Agents in Chemical Synthesis.

1. *Replacement of NH_2 by Cl, Br, I, CN, CNO, or CNS.*—Griess's researches on the production of the halogen derivatives of the aromatic hydrocarbons are now only of historical interest, since the methods commonly employed at the present time are due to Sandmeyer (*Ber.*, 1884, xvii., 2650) and to Gattermann (*Ber.*, 1890, xxiii., 1218; 1892, xxv., 1074). The latter of these investigators also extended the scope of this synthetical process by demonstrating that the cyano (CNO) and thiocyno (CNS) radicles could also be introduced into the aromatic nucleus by the use of the appropriate diazonium salt.

The course of the reaction between diazonium derivatives and cuprous salts (Sandmeyer) or copper powder (Gattermann) has been recently reviewed by Hantzsch (*Ber.*, 1900, xxxiii., 2544), whose conclusions may be summarised as follows:—

The course of the Sandmeyer reaction is not a simple one, and the final result is due to the simultaneous effect of three concurrent actions:—(i.) The formation of a labile diazonium cuprous double salt, which subsequently undergoes decomposition in such a manner that the radicle originally attached to copper migrates to the aromatic nucleus; (ii.) a catalytic action, which becomes the main reaction when copper powder is employed, whereby nitrogen is eliminated from the diazo-salt, so that the acid radicle becomes directly attached to the aromatic nucleus; (iii.) the formation of azo-compounds, which is accompanied by the oxidation of the cuprous salt to the cupric condition.

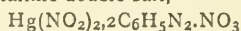
The concurrent effect of the first two reactions was demonstrated by subjecting dry *p*-bromobenzenediazonium bromide to the action of cuprous chloride dissolved in methyl sulphide. The product consisted chiefly of *p*-bromochlorobenzene mixed with a little *p*-dibromobenzene.



Cuprous bromide and *p*-bromobenzenediazonium chloride yielded *p*-dibromobenzene containing a little *p*-bromochlorobenzene. In both cases the first reaction predominates, and it may, under certain conditions, prevail to the almost complete exclusion of the second. Cuprous iodide, for example, gave rise to iodo-derivatives only, with various diazonium chlorides and bromides, and, on the other hand, the interaction of cuprous chloride and benzenediazonium iodide furnished chlorobenzene unaccompanied by iodobenzene.

2. *Replacement of NH_2 by NO_2 .*—The introduction of nitroxyl through the agency of the diazonium salt was first indicated by Sandmeyer, and further exemplified by Hantzsch (*loc. cit.*) in the following experiments:—

(i.). The crystalline double salt,—

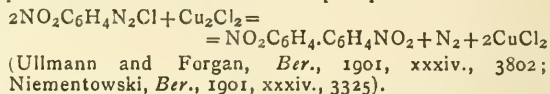


(melting-point 76°), obtained by mixing solutions of benzenediazonium nitrate and potassium mercuric nitrite, decomposes on boiling with water, yielding phenol and nitrophenol, but when treated with copper powder it furnishes a quantitative yield of nitrobenzene. (ii.). The diazonium sulphates, when mixed with a freshly prepared

suspension of cupro-cupric sulphate and treated with excess of an alkali nitrite, give rise to the corresponding nitro-derivatives; 2 : 4 : 6-tribromobenzenediazonium sulphate, for example, gives a 65 per cent yield of 1-nitro-2 : 4 : 6-tribromobenzene.

β -Nitronaphthalene, a substance prepared with considerable difficulty by other processes, is produced from β -naphthylamine to the extent of 25 per cent by this method, whereas Sandmeyer, who employed cuprous oxide and the diazonium nitrite, obtained only 7 per cent (*Ber.*, 1887, xx., 1497).

3. *Formation of Conjugated Systems RR or $R.N : N.R$.*—The third reaction signalled by Hantzsch may be rendered more apparent by reversing the usual order of mixing and adding the cuprous chloride dissolved in hydrochloric acid to the cold solution of the diazonium salt. Under these conditions, aniline, *o*-chloroaniline, and the *o*- and *p*-toluidines give rise to appreciable quantities of azo-compounds. The nitrated amines, however, behave very differently, yielding diphenyl-derivatives; this result being obtained with the three nitranilines, *o*-nitro-*p*-chloroaniline and *o*-nitroaniline-*p*-sulphonic acid.

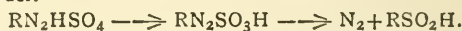


This type of condensation is also brought about by the use of cuprous oxide in ammoniacal or hydroxylamine solution (*Annalen*, 1902, cccxx., 122).

4. *Introduction of the Sulphonic Radicle SO_3H .*—The replacement of NH_2 by SH was first accomplished by Leuckart (*Journ. Prakt. Chem.*, [2], xli., 218), who treated the diazonium salt with an alkali xanthate and hydrolysed the resulting aromatic xanthate, thus obtaining either the thiophenol or the disulphide produced by oxidation. Either of these products yields the corresponding sulphonic acid on treatment with alkaline permanganate solution (F. Bayer and Co., *D.R.P.*, 70286; Wynne and Bruce, *Trans.*, 1898, lxxiii., 738).

The production of sulphinic acids by the direct action of sulphurous acid on diazonium salts appears to have been first observed by Müller and Wiesinger (*Ber.*, 1879, xii., 1348). A simple process, due to Gattermann (*Ber.*, 1899, xxxii., 1136), was accidentally discovered during an investigation of *o*-methoxybenzenediazonium chloride, when it was found that this salt on treatment with sulphurous acid yielded a diazonium sulphite which, on mixing with copper powder, evolved nitrogen, giving rise to the corresponding sulphinic acid; this product being subsequently oxidised by means of permanganate solution.

In general, the reaction takes place most readily with the diazonium sulphate, a cold solution of this salt in a large excess of dilute sulphuric acid being saturated with sulphur dioxide, and finally treated with copper powder.



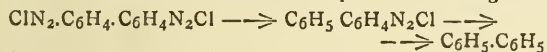
In the case of the diazotised naphthylamines it is better to add their solutions to the mixture of reduced copper and sulphurous acid.

These processes for the production of sulphonic acids have not, however, been successfully applied to the diazonium salts derived from the nitrated aromatic amines.

5. *Replacement of the Diazo-radicle by Hydrogen.*—The method originally employed for the elimination of the diazo radicle consisted in boiling the diazonium chloride with absolute alcohol; this operation does not, however, invariably give the required result, and Hantzsch (*Ber.*, 1901, xxxiv., 3337) has accumulated evidence in support of the view that the normal decomposition of a diazonium salt by an alcohol leads to the production of an alkyl phenoxide. Benzenediazonium chloride or sulphate when boiled with methyl alcohol yields anisole unaccompanied by benzene. Increase in the molecular weight of the alcohol or the accumulation of negative substituents in

the aromatic nucleus diminishes the yield of ether and augments that of the hydrocarbon. The benzenediazonium salts, when treated with ethyl alcohol, yield phenetole and a trace of benzene; their chloro- and bromo-derivatives, when boiled with this reagent, give halogenated benzenes but no substituted ethers, whereas methyl alcohol converts them into mixtures consisting chiefly of the substituted phenoxide and a small quantity of the halogenated hydrocarbon. Numerous examples of this reaction will be found in the work of Remsen and his pupils (*Amer. Chem. Journ.*, xv., 105; xix., 531, 547, 561).

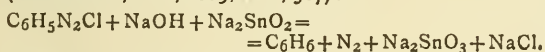
In the case of diphenyltetrazonium chloride the elimination of the diazonium radicle takes place in two stages.



(*Ber.*, 1898, xxxi., 479).

The reversion to the parent hydrocarbon is more readily effected by the process introduced by Baeyer and Pfizinger (*Ber.*, 1885, xviii., 90, 786; compare Wynne and Bruce, *loc. cit.*), which consists in reducing the diazonium salt to the hydrazine with stannous chloride, and subsequently removing the hydrazino-radicle $\text{NH}\cdot\text{NH}_2$ by boiling with cupric sulphate solution.

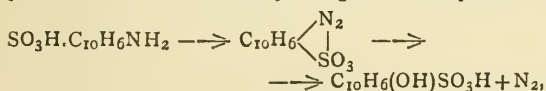
Sodium stannite has been recommended as an agent for reducing the diazonium salt to the hydrocarbon (Friedländer, *Ber.*, 1889, xxii., 587):—



Mai has recently found that *p*-toluenediazonium chloride, when added to a strong solution of hypophosphorous acid, gives rise to toluene, the yield being 67 per cent. Benzenediazonium chloride yields a mixture of benzene (two parts) and diphenyl (one part), whilst diazotised benzidine and α -naphthylamine furnish diphenyl and naphthalene respectively (*Ber.*, 1902, xxxv., 162).

6. *Substitution of NH_2 by OH .*—The replacement of NH_2 by OH , although an extremely important synthetical operation, can hardly be included amongst the modern developments of the application of diazonium salts, inasmuch as the process still employed, which consists in boiling the aqueous solution of the diazonium salt, is a legacy derived from Griess's pioneering researches.

The manufacture of the 1:4- and 1:8- α -naphtholsulphonic acids from the corresponding amino-compounds—

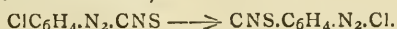


and the production of 1:8-dihydroxynaphthalene 3:6-disulphonic acid (chromotrope acid) may be cited as examples of the application of this process.

7. *Miscellaneous Substitutions.*—There are several other modes of reaction which, although of less importance from the synthetical point of view, are nevertheless of interest as indicating the extremely reactive character of the diazonium salts.

(i.). The amino groups in certain azo-derivatives of β -naphthylamine are replaced by the acetoxy-radicle when these substances are diazotised in warm glacial acetic acid (Meldola and East, *Trans.*, 1888, liii., 460) and Orndorff (*Amer. Chem. Journ.*, 1888, x., 368) showed that this reaction may be generally employed in the production of aromatic acetates.

(ii.). A remarkable example of intramolecular change was noticed by Hantzsch in studying the chloro- and bromo-diazonium thiocyanates (*Ber.*, 1896, xxix., 947; 1898, xxxi., 1253). These salts, when dissolved in alcohol containing a trace of hydrochloric acid, become converted into the isomeric thiocyanobenzenediazonium chlorides and bromides,—



This change takes place only when the halogen atom is

situated in an ortho- or para-position with respect to the diazonium group; transformation does not occur in the case of *m*-chlorobenzenediazonium thiocyanate.

The extent to which this rearrangement is possible is best indicated by the limiting case, 2:4:6-tribromobenzenediazonium sulphate in the presence of excess of potassium thiocyanate actually giving rise to 2:4:6-trithiocyanobenzenediazonium thiocyanate $(\text{CNS})_3\text{C}_6\text{H}_2\text{N}_2\cdot\text{CNS}$.

(iii.). Another extremely interesting case of molecular rearrangement is the conversion of the bromodiazonium chlorides into the isomeric chlorodiazonium bromides (Hantzsch, *Ber.*, 1897, xxx., 2334; 1900, xxxiii., 505; and *Journ. Prakt. Chem.*, xxvii., 98).

This transformation, which has been studied quantitatively, is a mono-molecular change, subject to the following laws:—

1. The bromine atoms undergo replacement only when present in the para- or ortho-position with respect to the diazo-radicle, those in the ortho-position being most readily removed. Metabromo-derivatives are not affected.

2. The ease of transformation increases with the number of bromine atoms present.

3. The transformation constant, calculated from the equation $\kappa = 1/t \log a/(a-x)$, increases with the temperature, and is also influenced by the solvent, having its minimum value in water, and becoming greater as the series of alcohols is ascended.

The diazonium salts containing two bromine atoms are stable when dry, but rapidly undergo conversion in ethyl alcohol; 2:4:6-tribromobenzenediazonium chloride becomes transformed even in the dry state.

(iv.). Dibenzoylhydrazines $\text{RN}(\text{COC}_6\text{H}_5)_2$ are obtained by treating diazonium salts with an aqueous suspension of benzoyl chloride and copper powder (*Ber.*, 1902, xxxv., 1964).

(To be continued).

THE ALKYLATION OF SUGARS.*

By THOS. PURDIE, F.R.S., and JAMES C. IRVINE, B.Sc., Ph.D.

THE method of alkylating hydroxyl groups by means of a mixture of silver oxide and alkyl iodides does not appear directly applicable to aldoses or ketoses, and results in oxidation and subsequent changes of some complexity. By means of this reaction, however, the authors have succeeded in alkylating methyl glucoside with the formation of tri-methyl and tetra-methyl methyl glucoside ethers, compounds from which alkylated aldoses can presumably be obtained on hydrolysis.

Tri-methyl Methyl Glucoside Ether.—The methyl glucoside used in the preparation was obtained by heating glucose in CH_3OH solution with HCl for fifty hours at 100° . The glucoside (melting-point $165-167^\circ$) was dissolved in boiling methyl alcohol, and a large excess of the alkylating mixture, in the proportion of two molecules iodide to one of oxide, gradually added. After all action ceased, the mixture was boiled under a condenser for over an hour, and filtered.

On removal of the alcohol, the filtrate was extracted with ether, and after drying and evaporation, the neutral syrupy extract was distilled in vacuum from a graphite bath. An extremely thick colourless liquid passed over between $155-157^\circ$ under 12 m.m. pressure, and after refractionation a sample gave on analysis figures in close agreement with the calculated numbers for tri-methyl methyl glucoside ether:—



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* Read before the British Association (Section B), Belfast Meeting, 1902.

A molecular weight determination showed that no rupture of the molecule had occurred, and the methoxyl content of the compound was confirmed by Zeisel determinations.

The higher fractions obtained in the vacuum distillation were extremely thick, and the results of analyses showed these to consist of incompletely methylated glucoside.

Tri-methylic methyl glucoside is optically active, a 5 per cent solution in alcohol showing a specific rotation of $+126.75^\circ$ at 20° , whilst for the pure substance $[\alpha]_D^{30} = +129.27^\circ$. The compound is soluble in water, alcohol, ether, and methyl iodide, and the aqueous solution is without action on Fehling until hydrolysed with HCl, when the aldose produced in the reaction effects ready reduction.

Tetra-methylic Methyl Glucoside.—This compound was prepared by adding silver oxide to a solution of the tri-methylic ether in a large excess of methyl iodide, and boiling the mixture for several hours. After filtering and evaporating, the product was distilled in vacuum, and tetra-methylic methyl glucoside obtained as a colourless fairly mobile liquid, boiling at $144-145^\circ$ under 17 m.m. pressure. In different preparations the boiling-point was the same, and satisfactory results were obtained in the combustions and Zeisel determinations. The specific rotation at 20° of the pure substance proved to be $+127.88^\circ$, whilst a 5 per cent solution in alcohol gave $[\alpha]_D^{20} = +127.78^\circ$.

Hydrolysis of the Compounds.

Both tri-methylic and tetra-methylic methyl glucoside when hydrolysed give compounds capable of reducing Fehling's solution, and therefore probably containing an "aldose" structure. On hydrolysis of the tri-methylic ether by means of 20 per cent HCl, a colourless gum was isolated from the reaction products, which, after drying at 110° , gave figures on combustion approximating to those required for tri-methyl glucose. The substance reduced both Fehling's solution and an ammoniacal solution of silver nitrate, and a qualitative Zeisel experiment showed that the methoxyl groups had survived the hydrolysis. So far this body has not been obtained in a state of purity, but we are at present engaged in the preparation of the compound on a larger scale, with a view to examining its properties and investigating the special reactions of which it is capable. We likewise hope to publish shortly an account of the alkylated glucose obtainable from the tetra-methylic methyl glucoside, and to continue our experiments on other alkylated sugars which are already partly prepared and examined.

Alkylation of Acetone-rhamnoside.

According to Fischer's formula for acetone-rhamnoside, the compound contains two hydroxyl groups, and we find that the silver-oxide reaction can be successfully carried out on the substance with the formation of di-methylic acetone-rhamnoside.

The rhamnoside, when dissolved in acetone, reacted energetically with silver-oxide and methyl iodide, and after filtration and evaporation the product was distilled in vacuum. Complete alkylation was, however, only obtained by dissolving the distilled product in methyl iodide and repeating the treatment with silver-oxide. On distillation, a colourless pleasant-smelling oil was obtained (boiling-point = $115-118^\circ$ under 11 m.m. pressure), which the combustion and Zeisel results showed to be di-methylic acetone-rhamnoside.

The compound is soluble in the ordinary organic solvents, and has scarcely any action on Fehling until hydrolysed with HCl.

A five per cent solution in acetone had a specific rotation of -24.64° at 20° , this result being in sharp contrast to the value of $[\alpha]_D$ for the parent substance, which equals $+17.4^\circ$.

Presumably the compound on hydrolysis splits off a molecule of acetone and gives a di-methylic rhamnose just as the rhamnoside itself yields acetone and rhamnose.

We are at present engaged in the investigation of this reaction, and it is our intention to examine the hydrolysis product in detail, with a view to establishing its reactions and constitution.

ON SUB-OXIDE OF LEAD.

By R. W. EMERSON MACIVOR, F.I.C., &c.,
Formerly Lecturer on Chemistry, Anderson's College, Glasgow.

REQUIRING some sub-oxide of lead in connection with an investigation in which I have been engaged, I adopted the method of making it used by Dulong, Boussingault, and Pelouze, viz., carefully heating lead oxalate in a retort from which air is excluded, but found the product to invariably contain a greater proportion of lead than theory required for the sub-oxide. Thus, in four different specimens the lead ranged from 96.89 to 98.36 per cent, theory demanding 96.28 (Pb=207). These irregularities in composition were undoubtedly due to the reduction of sub-oxide by carbon monoxide in the atmosphere of the retort.

Pelouze states that the oxalate should not be heated to a higher temperature than 300° , the heat being continued as long as any gas is given off. He found the gas thus evolved to consist of a mixture of CO and CO₂ in the proportions of 1 : 3 [$2\text{PbC}_2\text{O}_4 = \text{Pb}_2\text{O} + \text{CO} + 3\text{CO}_2$], excepting towards the end of the operation, when, particularly if "the heat be somewhat increased in order to finish the decomposition, the gas is richer in CO₂." This increase in the proportion of CO₂ can, of course, only arise from the reduction of Pb₂O.

I find that if a heated current of pure carbon dioxide be maintained through the retort during the decomposition of the lead oxalate so as to rapidly remove the CO immediately it is formed, and the temperature not allowed to exceed 300° , but kept rather a little under that point if anything, the final product is true sub-oxide free from PbO and metallic lead. It is a dull black powder tinged with grey, which bears lengthened exposure to dry air without undergoing change. Heated strongly— 350° or so—it alters in colour to greenish grey, being split up into Pb and PbO. It is not decomposed by water, but is acted upon by dilute alkalis and acids, and resolved into metal and PbO.

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THE LITMUS-PAPER TEST FOR MILK.

By H. DROOP RICHMOND, F.I.C.

In early text-books of chemistry an acid was wrongly, as we now know, defined as a substance reddening blue litmus-paper, and an alkali as a substance which turned red litmus-paper blue. An indicator is really a coloured salt of an acid having an ion of a different colour, and the behaviour of acids towards indicators depends on the relative dissociation constants of the acid and the indicator.

Indicators may be divided into classes, those which approach the limit of complete dissociation in a solution dilute enough to show the colour, those which approach the limit of no dissociation, and those intermediate, or, in other words, those whose acids are strong, weak, and medium.

Litmus is an indicator of the medium class, i.e., it is unaffected by weak acids, and incompletely affected by acids of medium strength.

Litmus-paper may be either red containing only the acid, or blue containing the acid with such an amount of alkali that no red ions are formed, or at some intermediate stage. If we test with these papers a partially neutralised mixture of acids of various strength, we may obtain quite contradictory results.

Phosphoric acid is a good example of three different acidities in one molecule; the first acidity is strong, the third is very weak, and the second is intermediate between the two, and about equal in strength to the acid of litmus. It has been shown that milk contains phosphates with the third acidity completely neutralised, and the second only partly so, and therefore milk is an excellent substance to show the peculiar behaviour of litmus.

If we take a blue litmus-paper and dip it into milk, the blue litmus having the acid completely neutralised is more alkaline than the milk, and the two tend to come into a condition of equilibrium by a portion of the alkali of the litmus passing to the milk; the consequence is that the litmus becomes less alkaline, and turns slightly red. If we take a red litmus-paper, which is more acid than the milk, alkali will tend to pass from the milk to the litmus, and turn it slightly blue. This is the so-called amphoteric reaction. A litmus-paper of some intermediate stage would be unaffected.

It is therefore quite fallacious to try and test the acidity of milk with litmus-paper; the old test to see if milk is sour by putting in a piece of blue litmus-paper has long been discarded by scientists, but unfortunately is still recommended by those who have the little knowledge which so often proves a pitfall; with a suitable litmus-paper all fresh milk can be condemned by this test, while, by judiciously changing the paper, milk which is on the turn can be triumphantly proved fresh.

THE PREPARATION OF GASEOUS PHOSPHIDE OF HYDROGEN.

By F. BODROUX.

AMONG the metallic phosphides, there are a certain number which, when treated with water or acids, give off phosphoretted hydrogen in a more or less pure state. Such is the case with the phosphide of calcium generally used in laboratories, and the same is also true with the phosphides of aluminium and magnesium.

M. Matignon (*Bull. Soc. Chim.*, vol. xxiii., p. 498) made use of the action of dilute acids on phosphide of aluminium for the preparation of gaseous phosphoretted hydrogen. As this latter compound is difficult to obtain we propose to replace it with a less pure compound, but one which has the advantage of being easily prepared in a few moments.

As intimate a mixture as possible is made, consisting of two parts of powdered aluminium and one part of red phosphorus; this can be set light to either directly or by the help of a sheet of paper on which it is placed. The combustion proceeds rapidly, with a brilliant yellow flame; fumes of phosphoric anhydride are given off, and a greyish mass remains behind; this consists of unchanged metal, with oxide and phosphide of aluminium.

When treated with cold water, this substance is decomposed slowly, and gives off pure phosphoretted hydrogen. The reaction is more energetic if we use warm water, but it must not be heated to above 50°, or the product obtained would contain traces of hydrogen. The proportion of this element will be greater as the temperature of the water approaches nearer to the boiling-point.

If an acid solution be used for this operation, the gas, which is given off very abundantly, will consist of a mixture of hydrogen and phosphide of hydrogen, from which the latter body can be separated easily by means of a hydrochloric solution of cuprous chloride.

In the preceding experiment the aluminium can be replaced advantageously by magnesium. A mixture is made of equal weights of magnesium powder and red phosphorus. The operation must be carried out with every care, using only small quantities at a time, or else, on account of the friction, the material might suddenly take fire. The mixture is set alight, and after the com-

bustion is over a yellowish substance remains, which is energetically decomposed by cold water, giving off pure phosphoretted hydrogen.

It is necessary, if we wish to collect the phosphide of magnesium with little trouble, to spread out the mixture of red phosphorus and the metal, in a thin layer over a large surface. The combustion will then take a little longer to be effected, and the loss of a small portion of the compound by projection is prevented.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 12.

THE DETECTION OF VERY SMALL QUANTITIES OF ARSENIC.

By GABRIEL BERTRAND.

In a previous paper on "The Existence of Arsenic in the Organism" (*Bull. Soc. Chim.*, Series 3, vol. xxvii., p. 848) I stated that I had so far perfected the method of detecting arsenic that I could detect a thousandth or even half a thousandth of a milligramme of this metalloid. In this paper I propose to give the details of the method and the precautions it is necessary to take to obtain such a result.

In the first place, the arsenic must be concentrated in a very small volume of liquid. I generally work with such quantities that at the end of the operation there is not more than from 30 to 60 c.c. of liquid in the hydrogen apparatus. It is quite by exception that the volume is sometimes double.

The apparatus must be then entirely freed from all trace of oxygen; without this precaution, a portion, or even the whole of the arsenic set at liberty, becomes oxidised, and passes into the state of arsenious acid, which is much more difficult or even impossible to detect. This is easily effected by forcing through the apparatus, all fitted up and charged with zinc, a good current of pure carbonic acid, such as may be obtained from bottles of liquid carbonic acid. The gas I used contained 0.08 per cent of oxygen. If we prefer to wash out the apparatus with the hydrogen produced therein, we are obliged to leave a notable quantity of acid liquor which will thus dilute the arsenical solution unless special means are taken to prevent this. Much time is saved, however, by proceeding as I have said. With a good current of carbonic anhydride, a few minutes is quite sufficient to get the apparatus perfectly free from oxygen, which result by the old method could not be obtained in less than an hour at the very least.

At the commencement of passing the gas the analysis tube is disconnected so that the gas may pass more easily.

When the apparatus is quite free from air a solution of one or two drops of dilute chloride of platinum in about 10 c.c. of one-fifth sulphuric acid is poured on the zinc, and we wait for about ten minutes before introducing the arsenical liquor.

Small glass tubes very finely drawn out are used as analysis tubes. If, for example, we are searching for quantities of arsenic, decidedly less than $\frac{1}{1000}$ th of a m.grm., it is advisable to use tubes having an internal diameter of not more than 1 m.m.

After having washed them with warm sulphuric acid or aqua regia, then with water, alcohol, and ether, they are completely dried, and cut to such a length that the end will be from 10 to 15 c.m. from the place where the ring will be formed; finally, this extremity is drawn out very fine for several centimetres to prevent the diffusion of air into the interior during the operation. If this precaution be not taken, very small deposits of arsenic would become invisible through oxidation as they were produced.*

* This oxidation even takes place with considerable rapidity in the cold, in the tubes in which the rings are kept, if we have not taken the precaution to seal them up full of dry hydrogen. Instead of an easily seen black deposit of the metalloid we only obtain a whitish trace of arsenious acid, sometimes imperceptible even on a black background.

It is not necessary to heat the analysis tube to a higher temperature than nascent redness, nor even, so it seems, along much of its length. However, in nearly all my experiments I used a row of small flames, about 20 c.m. in length, in preference to the flat Bunsen flame previously used.

It is advisable to dry the current of gas as it leaves the flask, by passing it through a column of cotton-wool previously heated to 110–120°. The cellulose thus dehydrated eagerly retains the watery vapour without acting on the composition of the gas.

Finally, to prevent the deposit of arsenic from spreading over too great a surface of the analysis tube, which can easily happen with capillary tubes having thick sides, it is as well to encourage the rapid condensation of the arsenical fumes, by surrounding the tube with a small refrigerator at some convenient place.

This latter may consist of simply a band of filter-paper, 4 or 5 m.m. in width; this strip of paper is wrapped round the tube two or three times and water falls on it, drop by drop, from a little reservoir above.

The excess of water runs off by the free end. The deposit of arsenic, collected thus in a small space, runs no risk of being overlooked. With quantities of the metalloid of over $\frac{1}{1000}$ th of a m.grm., and with tubes having thin sides, the use of the condenser is not necessary.

By taking all these precautions, as well as those already described by A. Gautier (*Ann. Chim. Phys.*, Series 5, vol. viii., p. 384), we are able to obtain a black ring, distinctly visible, of several millimetres in length, with as little as $\frac{1}{1000}$ th of a m.grm. of arsenic.

It will be easily understood that with a method of research of such delicacy, it is very difficult to obtain reagents free from arsenic. This is especially true of nitric acid. The purest I have been able to procure commercially, and which was prepared specially for me, still contained nearly $\frac{1}{1000}$ th of a m.grm. of the metalloid per kilogram. It was impossible to get completely rid of this arsenic by a series of simple distillations in a glass retort. It was only by three distillations, each time in the presence of one-tenth its weight of pure sulphuric acid, that this proportion could be reduced to less than $\frac{1}{600,000,000}$ th; that is to say, to no longer detect $\frac{1}{1000}$ th of a m.grm. in 600 grms. of the acid.*

During the research described above, I was also occupied with the destruction of organic matter. The method which gave me the best results was that of A. Gautier (*Comptes Rendus*, vol. cxxix., p. 936–938). The modifications which it has been recently proposed to make in this method, and which required a large quantity of acid, are unfavourable for the study of the arsenic normal to the organism. As I have made quite certain by direct experiments, and as can be seen from the attempts to purify reagents, there are always traces of arsenic carried over by the acid fumes; so that the modifications proposed, which give complete solutions of the organic matter, and which appear to be very good for the detection of appreciable quantities of arsenic, are of no use for infinitesimal proportions of the metalloid.

For example, on attacking 50 grms. of calves' liver, to which was added $\frac{1}{1000}$ th of a m.grm. of arsenic, with 10 grms. of sulphuric acid and 45 grms. of nitric acid in a first experiment, and with 50 grms. of sulphuric acid and 200 grms. of nitric acid in a second experiment, a ring was obtained representing approximately the amount of arsenic added in the first place, while there was nothing, or at best only the most doubtful trace, in the second case.

Instead of using nitric acid alone for the attack, I found it preferable to employ a mixture of 10 parts of nitric and 1 part of sulphuric acid. This mixture penetrates the

carbonaceous mass better, and, not being so volatile as nitric acid alone, it makes it possible, towards the end of the attack, to clean the warm sides of the crucible more easily. With the exception of this slight variation we proceed exactly according to A. Gautier's instructions; there is a little more sulphuric acid in the liquid extract, but that does not offer any inconvenience.

To detect traces of arsenic as small as those mentioned above, only thoroughly well digested products, quite free from organic matter, should be introduced into the Marsh's apparatus; this is a matter of very great importance.

When the precipitate, obtained by the action of the sulphydric gas, gives a brown solution with ammonia, charged with notable quantities of organic matter, the residue left must be attacked by the evaporation of the ammoniacal solution exactly in the same manner as the original material.

If the aqueous solution, separated by filtration from the hemic products, remains colourless, or nearly so, it is evaporated to dryness, and the residue dissolved in sulphuric acid at one-fifth is poured into the hydrogen apparatus. If, on the other hand, the aqueous solution is strongly coloured yellow, as happens occasionally when great care has not been taken in the destruction of the organic matter, it is necessary to precipitate the arsenic again by means of sulphuretted hydrogen.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 16.

THE MICROMETRIC ASSAY OF GOLD ORES.

By M. GUERREAU.

It often happens in the assay of poor gold ores, and of slimes, tailings, and other residues from the treatment of auriferous minerals, that the gold bead resulting from the assay, when placed in the balance, is so light that it cannot be weighed with any degree of accuracy. Harkort and Plattner (*Probirkunst*) measured the small beads, obtained by the cupellation of these ores, by means of two lines ruled on ivory similar to those in a Wedgwood pyrometer, and graduated by the help of spheres of gold of known weight.

The results obtained were not very exact, as the beads were flattened on one side and contaminated with silver. Goldschmidt proposed using a micrometer to measure the spheres, and Gozdorf (*CHEMICAL NEWS*, 1886) devised the method of forming the gold into a perfect sphere by fusing it in a bead of boric acid.

I have made a number of assays to check the correctness of this method, which, up to the present, has not been generally made use of in practical assaying.

The gold and silver bead is obtained in the ordinary manner, but the parting with nitric acid must be done with great care, so that the attack may proceed very slowly, and that if the gold is divided it may divide as little as possible. The flattened bead is placed in a small porcelain crucible, and treated with cold nitric acid of 1.18 density (22° B.) for about five minutes; next it is heated gently for ten minutes; then the temperature is raised, and it is treated for ten minutes with nitric acid of 1.29 (32° B.) density. If, at the commencement of the attack, too strong an acid or too high a temperature is used, the gold will be reduced to such a fine state of division that it would be difficult to avoid losses. It is then washed with water, decanted, and dried in the oven.

It is necessary to use a very gentle heat to drive off the last traces of moisture; in fact, if the water is driven off too rapidly, and above all if it is boiled, the gold will be disintegrated, and losses will occur.

As a general rule, inquartation is not necessary, as the silver contained in the assay litharge is amply sufficient.

A borax bead is melted in the blowpipe flame on a platinum wire, and, while still warm, it is pressed on the gold, which adheres to it firmly. On re-melting the bead

* The examination of the acid was effected by evaporating down 300 grms. with 20 grms. of pure sulphuric acid, added gradually, in a porcelain crucible. The evaporation is continued until only about 15 grms. of sulphuric acid are left; this is diluted with four parts of water, and after cooling transferred to the Marsh's apparatus.

the gold collects in the form of a sphere. It sometimes happens that two spheres of gold are obtained instead of one; it is impossible to make these two unite in the interior of the bead; in such a case the boric acid must be dissolved and the operation re-commenced. Although the great viscosity of the melted medium prevents the gold from becoming alloyed with the platinum, it is always advisable to make the borax bead as large as possible.

The boric acid is dissolved, and the sphere of gold measured under the microscope on a watch-glass. An enlargement of 100 to 150 times is most convenient for these assays, but the true value of the divisions of the ocular should be verified by means of a millimetre objective divided into 100 parts.

The sphere should be measured in six or eight different positions, and the mean of the values obtained taken. By operating in this manner, differences in diameter up to 0.03 m.m. have no appreciable influence on the results.

As a general rule, the spheres are very regular; the greatest variations I have observed were on a large sphere of 0.799 m.m. diameter, weighing 5.3 m.grms. The difference between the two extreme measurements were 0.036 m.m., or 4.5 per cent. On small spheres the difference is nil; if, however, too great a variation is found it will be necessary to re-melt the sphere. As a general rule, it may be said that the smaller the sphere the better are the results. It is not advisable to estimate quantities of gold of more than 6 or 7 m.grms. by this method, but on the other hand, there is, so to speak, no limit to the smallness of spheres of which the valuation is possible. The smallest sphere I have obtained weighed 0.04 m.grm. Gozdorf measured the very small spheres in the borax bead, but this method did not give me good results; as a matter of fact, fused boric acid is highly refrangible, and, further, a kind of luminous halo is formed round the sphere of gold, which interferes with the accurate observation of the edges.

The weight of a sphere of a substance of which the density is known is deduced from the formula—

$$W = \frac{\pi \times d^3 \times D}{6},$$

in which d represents the diameter of the sphere, and D the density of the substance; from this we get, $W = 10.123 \times d^3$, a constant with which we determine the weight of a sphere of gold having a diameter of one division of the micrometer. It only remains to multiply the figure thus obtained by the cube of the number of divisions of the sphere to obtain its weight. The sphere may be then weighed on the balance as a check. Gozdorf took 19.5 as the density of gold, but this figure gives results which are about $1\frac{1}{2}$ per cent too high. I used the density 19.33, determined by Gustave Rose, and which is generally accepted as the density of fused gold.

The following experiments set out in the accompanying table show the degree of accuracy which can be attained by this method. It will be seen that the differences per cent between the weights found on the balance and those by the micrometer seem considerable, but they are illusory

to a great extent, and are due principally to the impossibility of determining the twentieth and even the tenth of a milligramme with certainty on the balance. To prove this, I weighed together the spheres 3, 6, 7, and 8. The weight on the balance was 14 m.grms., the micrometric weight was 13.939 m.grms., or a difference of -0.43 per cent. To these spheres I added Nos. 2, 5, 12, and 13; the weight on the balance was 28.4 m.grms.; the micrometric weight was 28.355 m.grms., or a difference of -0.15 per cent.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 15.

PROCEEDINGS OF SOCIETIES.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Ordinary Meeting, October 7, 1902.

Mr. CHARLES BAILEY, President, in the Chair.

A PAPER on "The Reaction of Iodine with Mercuric Oxide" was read by Mr. R. L. TAYLOR.

In a former paper the author had shown that, when aqueous iodine is shaken up with precipitated mercuric oxide and rapidly filtered, the filtrate contained 80 to 90 per cent of the possible amount of hypoiodous acid. Messrs. Orton and Blackman have stated, in a paper read before the Chemical Society, that the solutions obtained from iodine and mercuric oxide contain only a small quantity of hypoiodite, the iodine existing mainly as iodic acid. Mr. Taylor concludes, from the description of these experiments, that Orton and Blackman were not aware of the extremely unstable nature of hypoiodous acid. They used ordinary powdered iodine, which is not sufficiently finely divided, and they took a great deal too long over their experiments. Using precipitated iodine, and performing the experiments as rapidly as possible, Mr. Taylor finds that, with ten to twenty-five times as much iodine in proportion to the water as he formerly used, the solution contains from 44 to 52 per cent of the possible amount of hypoiodous acid and very little iodic acid—results very different from those of Orton and Blackman.

NOTICES OF BOOKS.

Methods of Gas Analysis. By Dr. WALTHER HEMPEL, Professor of Chemistry in the Dresden "Technische Hochschule." Translated from the Third German Edition, and Considerably Enlarged, by L. M. DENNIS, of Cornell University. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1902. Pp. 490.

MANY important investigations in the field of gas analysis have been published in the interval that has elapsed since the appearance of the second edition of this work, and it is with the idea of bringing together these and his own experimental researches that the author has been led to prepare this third edition. The work has been thoroughly revised by both the author and the translator, and has been changed to such an extent that this translation may be regarded as a fourth edition of the book.

The additions comprise several new methods of collecting and keeping gas samples; determinations with the Honigsmann, Bunte, and Orsat apparatus; the new Hempel methods for exact gas analysis, new methods for the determination of combustible gases, the separation of argon from the atmosphere, improved methods for the determination of carbon monoxide in gas mixtures, the analysis of acetylene gas, the examination of gases pro-

No.	Diameter in hundredths of a m.m.	Weight on the balance in m.grms.	Micrometric, weight in m.grms.	Difference. Per cent.
1.	27.2	0.2	0.204	+2.00
2.	34.5	0.45	0.415	-7.77
3.	56.5	1.9	1.830	-3.68
4.	56.6	1.95	1.836	-5.84
5.	56.9	1.95	1.861	-4.56
6.	60.0	2.2	2.189	-0.50
7.	61.5	2.25	2.35	+4.53
8.	61.9	2.4	2.401	+0.04
9.	62.0	2.5	2.411	-3.56
10.	79.7	5.4	5.117	-5.22
11.	79.9	5.3	5.167	-2.51
12.	82.7	5.75	5.733	-0.33
13.	85.9	6.7	6.407	-4.37

duced by living bacteria, the simultaneous determination of fluorine and carbon dioxide, the determination of the heating power of gases, sulphur in organic substances, and the volumetric determination of carbon in iron, &c.

The book is divided into three principal parts and eighteen chapters; the third part on "Practical Applications of Gas Analysis" being of the greatest interest to analytical chemists, as it deals with the definite technical work required in many commercial operations, such as the manufacture of acetylene, sulphuric acid, bleaching-powder, saltpetre, and the nitric acid esters (nitro-glycerin, gun-cotton, &c.).

At the end of the volume is a number of tables useful in gas analysis.

The book is well arranged, and the descriptions of the various apparatus are clear and well illustrated; there is a good table of contents and an index.

Subject List of Works on Domestic Economy, Foods, and Beverages, in the Library of the Patent Office. London: The Patent Office. 1902. Pp. 136.

This list, which comprises works on the culture of cocoa, coffee, barley, hops, sugar, tea, and the grape, is arranged in a manner similar to those which have already been noticed in this column (CHEMICAL NEWS, vol. lxxxv., pp. 23 and 238). It includes a general alphabet of subject headings, with descriptive entries, in chronological order, of the works arranged under these headings; and a key or summary of these headings shown in class order. The present list comprises 1270 works, representing some 2043 volumes. The catalogue entries relating to these works number 1592, and are distributed under 174 headings and sub-headings.

Aids to Practical Dispensing. By C. J. S. THOMPSON, M.Pharm.Soc., Third Edition, Enlarged, with Illustrations. London and Dublin: Baillière, Tindall, and Cox. 1902. Pp. 92.

THE object of this work is mainly to lay before those students who have not had the opportunity of much practice, the various methods employed in dispensing medical prescriptions, and to enable them to become familiar with the necessary processes.

Special attention has been devoted to the more difficult operations, and practical hints are given in the making of emulsions, suppositories, and plasters.

The appendix contains, among other things, a list of the Latin terms used in prescriptions, with their English meanings, as well as a useful table of solubilities. There is a table of contents, and an index.

The Evolution of Artificial Mineral Waters. By WILLIAM KIRKBY, F.L.S., Lecturer on Pharmacognosy in the Owens College. Manchester: Jewsbury and Brown. 1902. Pp. 155.

THE object with which this book was written was to furnish a connected account of the initiation and development of the mineral water industry, which has achieved a more satisfactory position in England than in other countries, with the exception of America. Detailed technical descriptions of machines and processes have been avoided as much as possible, as the book is not intended as a manufacturer's handbook.

The first successful attempt to impregnate water with carbonic acid gas appears to have been made by Brownrigg in the year 1741, and later on Dr. Joseph Priestley devised a method for the more convenient use of this "new medicinal agent."

The application of the compression pump became quite common early in the nineteenth century, and in this country Bramah's machine has been found to be the only one giving a really continuous supply, though other makers have attempted to give a personal impress to their productions by adopting different designs,

An interesting development of the syphon is an adaptation which has made it possible to aerate the contents of the syphon directly by means of bulbs of condensed carbonic acid gas. These reservoirs are now generally known as "sparklets," and are looked upon as quite a new invention, but it is astonishing to read that they were invented and fully described so far back as 1874 by Arthur Marescot.

The book is profusely illustrated, and is provided with a good index.

In the copy before us there is a curious mistake; the frontispiece, "Priestley Exhibiting his Apparatus to the Fellows of the College of Physicians," has printed over it the medallion portrait of "Dr. Priestley, F.R.S.," which also faces p. 51.

Report of the Senior Analyst at the Cape of Good Hope, for the Year 1901. Cape Town: W. A. Richards and Sons. 1902. Pp. 61. With two Maps.

THE continuance of the war during the year 1901 brought about a temporary suspension of two important branches of the work of this department. The systematic investigation into the composition of the soils of the colony was entirely stopped, and the operation of the Adulteration Act has also been all but entirely suspended; however, in spite of these set-backs, the number of samples analysed during 1901 was only 559 less than in 1900; so that there is every indication that in branches not affected by the unsettled state of the country, the onward movement is as steady as ever. The actual number of samples analysed during the past four years is as follows:—

1898..	..	..	..	..	..	1650	samples
1899..	..	..	..	..	..	1903	"
1900..	..	..	..	..	..	1949	"
1901..	..	..	..	..	..	1389	"

Of these, the largest number of analyses during 1901 were of milk, viz., 566 samples; water, soils, fertilisers, tinned-meats, and ink are among the other materials which claimed most attention.

Beginners' Guide to Photography. Eighth Edition, Revised and Enlarged. London: Messrs. Perkin, Son, and Co., Ltd.

THE enterprising publishers of this "Guide" are to be congratulated for having collected together in a convenient form a mass of useful photographic information. At the present day when almost every schoolboy is a photographic aspirant, a little genuine instruction that will give an intelligent idea of the reasons for performing the various operations involved in making a photographic picture is of real value. Details of dry-plates, development, the chemicals used, stereoscopic photography, lantern-slide making, enlargement, &c., are given clearly and in a thoroughly practical manner. Unfortunately, there is neither a table of contents nor any index. This is a great pity, and detracts much from the usefulness of the book. There are 226 pages, of which 89 are devoted to advertisements, and we are glad to see that the latter are all together at the end and not, as in the case of some books, interleaved with the instructions.

Guide to Preparation Work in Inorganic Chemistry; for Students of Chemistry and Pharmacy. By Dr. REINHART BLOCHMANN, Professor at the University of Königsberg. Authorised Translation, by JAS. LEWIS HOWE, Washington and Lee University.

THIS book, written in the strictest fashion of American spelling, is intended to serve as a guide to students in inorganic preparation work. That the rational preparation of chemical compounds must always rest upon the equivalent proportions of the reacting substances is insisted upon; the time necessary for the various operations is indicated, and in cases where by-products are

formed the recovery of these in a useful form is carried out. The methods for the preparation of some twenty-five compounds are given with clear illustrations of the forms and disposition of the apparatus needed in each operation; while at the end of the book are tables of atomic weights, specific gravity, and solubility.

The book is issued by the Department of Chemistry, Washington and Lee University, Lexington, Virginia.

OBITUARY.

PROFESSOR HENRY MORTON, Ph.D.

WE regret to announce the death of Dr. Henry Morton, which occurred recently at Hoboken, New Jersey, U.S.A.

Dr. Morton has been well known for many years in connection with the Stevens Institute of Technology, Hoboken, of which he was the President from its foundation in 1871, in accordance with the will of the late Edwin A. Stevens.

Dr. Morton was the author of many scientific papers, his first one being on "An Important Adjunct to the Induction Coil," published in the *CHEMICAL NEWS* in 1867; in the following year he published two more papers, viz., "Sunlight and Moonlight," and "Resistance and Transmission of Motion," followed by the "Solar Eclipse of August 7th" in 1869.

He was the author of several papers on colour and fluorescence, and in conjunction with Prof. Carrington Bolton did some important and interesting work on "The Fluorescence and Absorption Spectra of the Uranium Salts" in 1874; another highly fluorescent body called "Thallene" was the subject of a paper published in 1876, in which Dr. Morton gave a description of its source and the history of its discovery.

Optical subjects, however, were not the only ones dealt with by Prof. Morton; in 1878 he wrote a paper on "The Singing Telephone at the Stevens Institute," and another "On the Elimination of Antimony from the Human Organism," while in 1879, in conjunction with Mr. W. Geyer, he published a paper entitled "Experiments illustrating the Formation of Fast-red or Rocceline," and another in 1880 on "A New Sulpho-Acid of Phenanthrene."

Though Prof. Morton's publications ceased in 1880, he by no means retired from active life at that date, but devoted his whole energies to the welfare of the Institute of which he has been so many years the distinguished head.

A Compound of Bromide of Aluminium with Bromine and Sulphide of Carbon.—V. A. Plotnikof.—If, to a solution of bromide of aluminium in sulphide of carbon, we add gradually a little bromine or a solution of bromine in sulphide of carbon, an oily liquor is formed at first, of a dark red colour, which, as the quantity of bromine added increases, becomes transformed into a yellowish-red solid body. When washed with pure sulphide of carbon and dried *in vacuo*, this body is in the form of a yellow amorphous powder, appearing greenish by reflected light; it rapidly becomes red when exposed to direct sunlight; a trace of moisture produces the same effect. It will remain for a long time without change when kept in sealed tubes in the dark; it melts at 86–90° with decomposition, leaving bromide of aluminium, $AlBr_3$; it is soluble in ether, sulphide of carbon, bromide of ethyl, bromide of ethylene, and benzene. Analysis indicates the composition $AlBr_3 \cdot Br_4 \cdot CS_2$. Water decomposes this body with the evolution of heat and the formation of a large quantity of gas; a deep red-coloured oil is produced which is easily transformed into the crystallised trithio-bromide, $C_2S_3Br_6$.—*Journ. Soc. Phys. Chim. R.*, vol. xxxiii., p. 91.

CORRESPONDENCE.

PROPOSED ELECTRO-CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—I notice in the *CHEMICAL NEWS* for October 3rd (vol. lxxxvi., p. 174), under the heading of "Notes and Queries," a query from Dr. Max Reuter enquiring whether there is a Society of Electro-chemists in London. Readers of the *CHEMICAL NEWS* may perhaps be interested to learn that there is a proposal on foot to form an Electro-chemical Society in this country. To this end, a small committee has been holding occasional meetings since March, and has recently sent out circulars to various chemists and others interested in electro-chemical science. A very fair response has been received; but I should like to point out, through the medium of the *CHEMICAL NEWS*, that the response has been mainly from those interested in the purely electrical side of the subject; chemists being inclined to hang back, in order, apparently, to see whether the Society can be formed before they will lend a helping hand. At the same time several prominent chemists have promised their support.

It is felt by those interested in the formation of the Society that electro-chemistry is not sufficiently known and applied in this country, and it is hoped that if an Electro-chemical Society is formed interest may be awakened, and both science and industry be the gainers. Germany and America have electro-chemical societies, France and Russia are experimenting and founding large industries. Our electricians desire to introduce new processes, but are largely handicapped by want of chemical knowledge; they want help from the chemists. The Society, if formed, should bring the chemists and electricians together, and both would benefit by the interchange of ideas.

I shall be very pleased to send particulars of the proposed Society to any chemists who may be interested in the subject; or they can obtain information from Mr. S. V. Simpson, Grosvenor Mansions, Victoria Street, who is Hon. Secretary to the Committee.—I am, &c.,

F. MOLLWO PERKIN.

Borough Polytechnic Institute, S.E.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 12, September 22, 1902.

Compounds of Silicon with Cobalt, and a New Silicide of the Metal.—P. Lebeau.—The analogy existing between the formulæ and properties of the two known silicides of cobalt and those of the silicides of iron, led the author to suspect the existence of a third compound, richer in silicon and comparable with Si_2Fe . His researches confirmed this prediction. Such a compound can be produced by heating cobalt in presence of an excess of molten silicon, or by the action of the temperature of the electric furnace on a mixture of copper silicide, cobalt, and silicon. In the latter case, the compound is better crystallised and more easily purified. Analyses made on various specimens of this substance show that it has the formula Si_2Co . It always contains, however, as an impurity, a little carbon silicide. It is found in the form of little dark coloured crystals, of density 5.3.

The Calorific Power of Oil.—M. Goutal.—The author endeavours to establish a relation between the calorific power of coal and that of combustibles which are

commonly used, by the process of calcination, incineration, and desiccation, in order to determine the fixed carbon, the volatile materials, the ash, and the humidity. His experiments show that the calorific power of pure anthracite has the mean value of 8250 cal., that of anthraciteous oils 8550 cal. A maximum of 8700 cal. is attained for coal where the volatile matter is from 10 to 30 per cent of the whole. The calorific power of oils increases in proportion as their volatile matter decreases, up to the limiting value of 30 per cent, after which the calorific power of natural combustible materials and that of their volatile matter diminishes concurrently.

MISCELLANEOUS

"Ore in Sight."—As a result of the discussion of a paper recently read before the Institute of Mining and Metallurgy by Mr. J. D. Kendall, the Council of the Institute recommend, among other things, that members should not make use of the term "Ore in Sight" in their reports, without indicating, in the most explicit manner, the data upon which the estimate is based; the term in question is frequently used to indicate both "ore blocked out" and "ore which may be reasonably assumed to exist" though not actually blocked out. In using the term "ore in sight" an engineer should demonstrate that ore so described is capable of being profitably extracted under the working conditions obtaining in the neighbourhood. May we suggest that the term "in sight" is probably a corruption of "*in situ*," which has a very different meaning, and would naturally be liable to misconception if used indiscriminately.

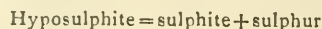
German Apparatus in New Zealand.—We have received from the Agent-General for New Zealand a cutting from *The Lyttleton Times*, in which Dr. Evans, of Canterbury College, gives a list of nine reasons why the chemical apparatus for use in the college should be obtained from German firms instead of English. These nine reasons form a scathing criticism of the business methods of English firms. Some of the reasons are as follows:—Many of the lines required are not made in England at all; the German goods are, as a rule, made of better material, and are very much better finished; the prices charged by most English dealers are exorbitant, and in no way represent the actual value of the goods supplied; the goods, when ordered from an English firm, very often prove to be of French or German make, but in addition the goods are not seldom seriously damaged by deliberate "tinkering" on the part of the English dealer; if articles are ordered "as per plan enclosed," the overseer of the German house will see that his workmen do work according to the plan, while many an English firm rests content if, after many days, it returns you something "distinctly resembling" your plan. Dr. Evans goes on to point out that it would be distinctly unfair to make such a series of charges without supporting them, where possible, with definite instances; this he proceeds to do in detail, quoting at first only instances which have come under his own personal observation, and confining himself, in the main, to the experience of the last three years only. In conclusion, Dr. Evans writes that it is but fair to state that the above criticisms, as a whole, do not apply to English electrical apparatus of the better class, nor is it difficult to get first-class work done, at a somewhat higher price it is true, in the optical and acoustical branches.

Decomposition of Hyposulphite of Sodium by Acids.—H. V. Ettingen.—It is well known that the addition of an acid to a solution of hyposulphite of sodium only causes a precipitate after the lapse of some instants. The author has devised an apparatus by which he can accurately determine the time which elapses between the mixing of the two liquids and the appearance of the precipitate; by this means he has been able to

ascertain that the time, y , depends on the concentration x , of the hydrogen ions in the acid liquor employed, the law of this dependence being represented by the equation—

$$y = \frac{1}{A \log (1 + b x)};$$

where A and b represent two constants. The time is therefore the same for isohydric acid solutions. The addition of a solution of sulphite of sodium retards the formation of the precipitate of sulphur; the relation between x and y keeps the same logarithmic form, but the values of the constants A and b depend on the quantity and the concentration of the sulphite added. The reactions observed by Colefax (*Chem. Soc.*, 1892, vol. lxi., p. 176 and 199) between hyposulphite and sulphite of sodium did not permit of the study of the state of equilibrium to which the reaction—



may give rise. Finally, the influence of the concentration of the ions of hydrogen in the acid liquor makes itself felt, not only on the time which elapses before the appearance of the first cloudiness, but also on the speed with which the precipitate continues to be formed; measurements of conductivity have, in fact, enabled it to be observed that this speed is the same in the cases of isohydric acid solutions.—*Zeit. Phys. Ch.*, vol. xxxiii., p. 1.

Electrolysis of the Alkaline Salts of the Organic Acids.—J. Petersen.—The electrolysis was done at 0° on slightly acid solutions of the potash salts of the acids under examination. Under these conditions, formate of potassium gave approximately equal volumes of hydrogen and carbonic acid (the result of oxidation at the anode), with a small quantity of oxygen. In dilute solutions the amount of carbonic acid obtained increases with the density of the current; in concentrated solutions the disengagement of oxygen at the anode almost ceases. Acetate of potassium gives ethane and hydrogen in proportions which vary with the strength of the current; carbonic acid gas is also given off at the anode; the formation of ethylene has not been observed, neither is there any acetate of methyl formed. Propionate of potassium gives butane, propionate of ethyl, ethylene, and carbonic acid gas at the anode, while hydrogen is given off at the cathode. Butyrate of potassium gives isopropyl alcohol, butyrate of isopropyl, hexane, and apparently butyrate of propyl; at the same time, the gaseous mixture obtained contains 1 volume of propylene for each 2 volumes of hydrogen. Finally, isobutyrate of potassium gives isobutyrate of isopropyl, isopropyl alcohol, and a little di-isopropyl, and, at the same time, hydrogen and propylene.—*Zeit. Phys. Chim.*, vol. xxxiii., p. 99.

JENNER INSTITUTE OF PREVENTIVE MEDICINE.

The Governing Body of the Jenner Institute of Preventive Medicine offers a STUDENTSHIP of the value of £150, tenable by a British Subject for one year, but renewable for a second year at the option of the Governing Body, for the purpose of Research in the Department of Chemistry at the Institute, under the direction of the Governing Body.

Applications to be sent in by October 22, 1902.

FRIDAY, OCTOBER 24th.

THE OIL & STEARINE COMPANY.

MESSRS. EDMUND W. RICHARDSON and SON will SELL BY AUCTION, at the MART, CITY, on FRIDAY, OCTOBER 24th, at TWO o'clock, the important WHARF AND MANUFACTURING PREMISES, Abbey Creek, West Ham. The Property comprises upwards of Two Acres, has a Water Frontage, communicating with the Thames, of about 413 feet, together with numerous Buildings, Foreman's House, &c. Lease sixty-one years unexpired, at a moderate ground rent.

May be Viewed and Particulars, with Conditions of Sale and Plan, had of Messrs. FOSTER, SPICER, and FOSTER, Solicitors, 7, Queen Street Place, E.C.; and at the SURVEY and AUCTION OFFICES, 50, Finsbury Square, E.C.

THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2239.

THE RADIO-ACTIVITY OF URANIUM.

By FREDERICK SODDY.

DURING the course of the investigation contained in the preceding paper on the radio-activity of thorium, it became advisable to investigate in parallel a radio-active element that does not give out an emanation, or excite radio-activity upon surrounding bodies. It has been shown that these secondary actions always form a possible factor in the results obtained with thorium. For this purpose the radio-activity of uranium was chosen, but at the outset great differences arose between the results obtained and those published in the same field by prior investigators. These differences led to a comparative study being made in certain cases of the photographic and electrometer methods of measuring uranium radio-activity, which resulted in an explanation of the anomalous results that had been obtained.

Sir William Crookes (*Proc. Roy. Soc.*, 1900, p. 409) made the beautiful discovery that in one chemical operation uranium could be obtained inactive to the photographic plate, while the whole of the inactivity was concentrated in a small non-uranium residue. This residue, to which he gave the name U.X, was at least a hundred times more active than the uranium from which it had been separated.

On repeating this separation, which consists in precipitating solutions of uranium with ammonium carbonate, and re-dissolving the precipitate in excess of the reagent, it was found that the small residue of UrX was almost inactive, while the uranium, contained in the ammonium carbonate filtrate, possessed about the normal amount of activity. The electrical methods of Professor Rutherford were employed for measuring radio-activity. The same negative result was obtained by the other method of separation employed by Crookes. If crystallised uranium nitrate is dissolved in ether, the uranium divides itself in two unequal fractions between the ether and water present. That dissolved in the ether layer, which is the major fraction, was found by Crookes to be inactive to the photographic plate, while the small part dissolved in the aqueous layer possessed all the activity contained in the original uranium nitrate. But as in the former case, on repeating the operations, both fractions appeared almost equally active to the electrometer, and no separation had apparently been effected.

The same preparations were then examined for their action on the photographic film, and gave results exactly the converse of those observed with the electrometer and in accord with the published results of Sir William Crookes.

Rutherford (*Phil. Mag.*, 1899, p. 109) showed that uranium radiation consists of two different types, which he named the α and β radiation. The α is absorbed very readily even by gases, being reduced to half value by passage through 4.3 m.m. of air. The β , on the other hand, is very penetrating in character, and is but little absorbed by gases. It is able to pass through 0.5 m.m. of aluminium before it is reduced to half value. This latter part constitutes only a few per cent of the total radiation of the uranium. In addition, by the electrometer method of measurement under ordinary circumstances, a fraction only of the intensity of the β radiation is recorded, for this method depends upon the ionisation of the air, and this is proportional to the absorption of the rays by the air. It follows, therefore, that under ordinary circumstances, in which the rays traverse a few centimetres only of air,

that the electrometer method measures practically the α radiation of uranium alone. The photographic method employed by Crookes, in which the rays are made to pass through glass or card before reaching the sensitive film, will, on the other hand, measure only the β radiation. Hence the results obtained would be explained if the methods employed separated the β radiation only, and left the α radiation intact.

Becquerel has shown (*Comptes Rendus*, 1900, cxxx., p. 1584) that the rays from uranium are deflected in the magnetic field, and therefore consist of cathode rays. Rutherford and Grier (*Phys. Zeit.*, 1902), in a general investigation of the rays from various radio-active substances to determine what proportion in each case was deviable in the magnetic field, and therefore cathodic in nature, had already at this time shown that the β radiation of uranium is entirely cathodic, and the α radiation not at all. They undertook the examination of the specimens that had been prepared in the course of the present work, the details of which appear in their paper with the special apparatus employed. It suffices to state here that in the arrangement they adopted the rays are made to pass through a sufficient thickness of air to absorb a considerable part, and the sensitive Dolezalek electrometer was employed. Under these circumstances UrX was found to be giving out ionising rays abundantly. This radiation was shown to be the β radiation of uranium only, practically free from α , for it passed through aluminium foil without great loss, and is deviable to the same extent by the magnetic field. The rays from the photographically inactive uranium was found, on the other hand, to consist entirely of α radiation, and gave no rays deviable in the magnetic field, or capable of passing through thin aluminium foil. I must here express my great obligation to Professor Rutherford and Mr. Grier for permission to use these results.

It thus appears that the methods of chemical separation employed by Crookes effect a separation only of the constituent responsible for the β radiation. The uranium after the process still retains the whole of the non-deviable radiation, which in the electrometer method contributes the greater part of the effect. In this respect uranium is analogous to thorium, as shown in the preceding paper. But the excited radio-activity produced by ThX as a secondary effect, which itself comprises both deviable and non-deviable radiation, makes it impossible at present to say whether the primary radiation of ThX is, like that of UrX, wholly cathodic or not. The non-separable parts in both cases consist entirely of rays non-deviable in the magnetic field.

The next point to be decided was whether the α radiation of uranium could affect the photographic plate. A sample of the preparation free from β radiation was exposed about 5 m.m. away from a sensitive film for seventy-two hours without intervening screen. Only a very slight darkening occurred, so that the action, if any, of the α radiation may be considered negligible in comparison to the effect of the β radiation. It is not possible to try longer exposures than three days by this method, owing to the regeneration of the β radiation which will be referred to later. However, Becquerel (*Comptes Rendus*, 1902, cxxiv., p. 208) exposed plates for twenty and forty-nine days near uncovered uranium salts, in a magnetic field where the β radiation would be deflected and eliminated, and failed even after these long periods to obtain an impression on the sensitive film. He concluded that the whole of the uranium radiation is cathodic, and can be deflected by the magnetic field. But the foregoing considerations make it clear that the α or non-deviable radiation of uranium, which contributes the major part of the ionisation effect, is without appreciable action on the photographic plate.

In light of these results, and those obtained for thorium in the preceding paper, the method employed by Becquerel (*Comptes Rendus*, 1900, cxxxi., p. 137) to separate the active constituent of uranium is of interest. M. Becquerel

precipitated barium as sulphate in solutions of uranium, and found that after successive precipitation the activity of the latter was much enfeebled, both towards the electrometer and the sensitive film. As, however, he enclosed the salt in paper for the electrometer measurements, and this absorbs the α radiation almost or quite completely, the result must not be taken to mean that both the α and the β radiations were separated by the process. On repeating the separation it was found that, as in the case of the methods of Crookes, the β radiation only was removed. After four successive precipitations in one day, the β radiation was found to be reduced to 8 per cent of its original value, and eight more precipitations on the day following completely removed it. But the activity of the resulting uranium preparation to the electrometer under ordinary circumstances was hardly appreciably decreased. The α radiation had therefore not been affected.

Becquerel has already shown (*Comptes Rendus*, 1901, cxxxiii., p. 977) that the uranium after this treatment recovered its normal activity on standing. With the sensitive electrometer the presence of cathode rays in a product originally quite freed from them, can be detected after three days. It thus appears probable that what has been shown to hold true for ThX applies equally to UrX, and the subject is under investigation conjointly with Professor Rutherford. The same question therefore arises for the non-separable activity of uranium already discussed for that of thorium.

1. Is this residual activity to be regarded as a secondary radiation produced by the presence of UrX?
2. Or, is it caused by a distinct material substance capable of chemical separation?

On the first view, if UrX—the cause of the phenomenon—is removed, the residual activity will decay with time. The following experiment was therefore performed:—The solution of uranium nitrate which had been successively precipitated with barium sulphate twelve times, and had been shown to be free from β radiation, was allowed to stand. Every three or four days it was once more precipitated in the same manner, and the UrX produced during that period removed from the uranium. After twenty-one days, the uranium in the solution was precipitated with ammonia and converted into the green oxide. For comparison, a sample of the same uranium nitrate, as obtained from the maker, was subjected to two precipitations with barium sulphate to remove most of the β radiation, the uranium then being precipitated and converted into oxide as in the former case. The radiations from the two samples were then directly compared. In the one the α radiation had been given three weeks to decay, and by comparison with the other a direct measure of the diminution suffered during this period could be obtained. Not the least difference, however, could be detected in the intensities of the radiations in the two cases. The actual values obtained were within 1 per cent of each other. If it is assumed that in this experiment a difference of 5 per cent could be with certainty detected, the conclusion is arrived at that if the α radiation of uranium is a secondary phenomenon produced by the β , it takes at least a year to decay to half value. As this is not in accordance with what is known of the nature of excited radio-activity, the view cannot be regarded as probable.

On the second view, the α radiation is produced by a second distinct type of matter. But as in the case of thorium, all attempts made to separate such a constituent of uranium by chemical methods have so far failed, although the methods have not yet been exhausted. It is, however, interesting to note that polonium, discovered by Curie, fulfils in almost all respects the functions of this hypothetical constituent. It gives only non-deviable radiation, and Professor Rutherford to whom the suggestion is due, found that the penetration power of the rays from polonium is very similar to that of the uranium radiation. Moreover, M. and Mme. Curie (*Comptes Rendus*, 1902, cxxxiv., p. 85) have stated that its

activity slowly decays with time, which is to be expected *after*, but not *before*, it has been separated from the uranium producing it. However, experimental work has not yet justified this suggestion.

The actinium of Debierne, according to a recent paper by Crookes (*CHEMICAL NEWS*, lxxxv., p. 109), has been found to be identical with UrX, although no reference is given.

In the paper just quoted, Crookes brings forward some results obtained by the photographic method which led him to the conclusion that UrX gives a radio-active emanation similar to that given by thorium and radium. No evidence of such a radio-active emanation has been obtained in the course of the present work even with the most sensitive electrometer, and it appears probable that the cause of the darkening of the photographic plate by this body in the cases where the film is shielded from direct radiation, is not a radio-active substance in the accepted sense of the word, but an agent similar to hydrogen peroxide in its photographic actions.

Macdonald Chemistry and Physics Buildings,
McGill University.

ON PERCHLORIC AND PERIODIC ACIDS.

By A. ASTRUC and H. MURCO.

THE thermochemical examination of perchloric and periodic acids has shown that singular differences exist between these two bodies. Thus, perchloric acid behaves as a strong acid, decidedly monobasic, giving off 14.25 cal. with soda, with complete solution; an excess of base or acid has no sensible influence on the neutral salt, and the perchlorates are very stable.

Periodic acid behaves differently; according to the amount of potash used for its neutralisation it gives off variable quantities of heat, so that MM. Basarow, Thomsen, and Berthelot all regarded it as a bibasic acid, with a manifest tendency to form not only acid salts, but also basic salts containing up to 5 atoms of a monovalent metal.

Ferlund looked upon periodic acid as being tribasic, Rammelsberg tetrabasic, while Langlois and Leutsch thought it was pentabasic.

The comparative examination of the action exercised by these two acids on some of the colouring reagents generally used in acidimetry, gave us results of a similar kind.

Our experiments were carried out on the hydrate of perchloric acid, $\text{ClO}_4\text{H}_2\text{H}_2\text{O}$, and the hydrate of periodic acid, $\text{IO}_4\text{H}_2\text{H}_2\text{O}$, the composition of both of which was previously verified by analysis.

With the following indicators, viz., heliantine A, phenolphthalein, Poirrier's blue, tincture of litmus, and rosolic acid, the hydrate of perchloric acid behaved as an exactly monobasic acid; the reactions were quite sharp.

The hydrate of periodic acid behaved altogether differently. In the presence of heliantine A it is saturated by one molecule of potash, soda, or ammonia, and by half a molecule of lime, baryta, and strontia; the reactions are sharp and very distinct.

The results obtained are very different if we use phenolphthalein; in this case the reactions are progressive, generally uncertain, and vary with the alkaline solution used. The rose colouration of the reagent appears after the addition to one molecule of periodic acid, of 1.5 to 1.7 molecules of potash, soda, or ammonia; under the same conditions, two molecules of acid require 1.9 to 2.0 molecules of baryta and 2 to 2.3 molecules of strontia and lime.

Litmus and rosolic acid both give results similar to the above, but the reaction is still less distinct; Poirrier's blue gives results practically agreeing with those obtained with phenolphthalein.

The thermochemical observations are thus confirmed

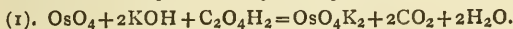
by these alkalimetric experiments. Perchloric acid is a strong acid comparable with hydrochloric acid, nitric acid, &c. Periodic acid is a complex acid possessing various acid functions, one which acts on heliantine A being strong, and the others weaker and influencing the other indicators.

A further result of these experiments is that all these colouring agents can be used for the titration of perchloric acid, and only heliantine A should be used with periodic acid.—*Bull. Soc. Chim.*, Series 3, vol. xxvii, No. 18.

THE COMPLEX SALTS OF OSMIUM. OSMYLOXALATE OF POTASSIUM.

By M. VÈZES and L. WINTREBERT.

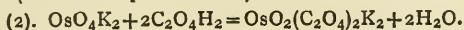
I. Action of Oxalic Acid on a Potassic Solution of Peroxide of Osmium.—If crystallised oxalic acid is added gradually to a solution of peroxide of osmium in potash-lye, keeping the mixture at boiling-point in a flask fitted with a vertical condenser, the following phenomena are successively noticed:—First of all, the potash and the peroxide being in excess with regard to the oxalic acid, we observe that the mixture, which is coloured a deep brownish red at first, takes the reddish violet tint characteristic of solutions of osmiate of potash, OsO_4K_2 , and at the same time carbonic acid is given off; the oxalate of potassium formed in the solution thus plays the part of a reducing agent under these conditions, and acts on the peroxide of osmium in the same manner as alcohol or nitrite of potassium in the classic methods of preparing osmiate of potassium, described for the first time by M. Fremy (*Ann. Chim. Phys.*, 1844, Series 3, vol. xii, p. 516). The reduction which takes place in the solution can be represented by the equation:—



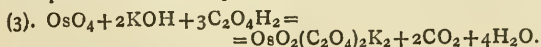
If we increase the amount of oxalic acid used, we observe the appearance of a black pulverulent precipitate in the body of the violet liquor; this is, according to all appearance, the osmic acid, OsO_4H_2 , described by Moraht and Wischin (*Zeit. Anorg. Ch.*, vol. iii, p. 156). This body, which is always formed when we have an osmiate in acid solution, takes its rise in this case from the presence of a slight excess of oxalic acid over the quantity corresponding to equation 1.

The addition of a further quantity of oxalic acid has the effect of re-dissolving this precipitate and giving an opaque solution of a blackish brown colour, which finally, if kept at the boiling-point with the addition of a sufficient excess of oxalic acid to give the solution a distinctly acid reaction, becomes almost decolourised, forming a bright yellowish-brown solution.

On cooling, this solution deposits brown crystals, having under the microscope the appearance of fine birefrangible prismatic needles. As we shall see later on, the composition of these crystals can be represented by the formula $\text{OsO}_2(\text{C}_2\text{O}_4)_2\text{K}_2 \cdot 2\text{H}_2\text{O}$, and we have given them the name of osmyloxalate of potassium. This salt is the result of the following reaction between the osmiate (or osmic acid) first formed, and the excess of oxalic acid used (or its monopotassic salt):—



Disregarding the intermediate products, the following equation, obtained from equations 1 and 2, expresses the formation of the same salt from the primary materials first put into reaction—peroxide of osmium and potash:—



Of the two reactions 1 and 2, which go to form osmyloxalate of potassium, the second takes place very rapidly; we shall see later on that a solution of osmiate of potas-

sium, treated with an excess of oxalic acid, gives almost immediately an abundant deposit of osmyloxalate. On the other hand, the first of these reactions, the reduction of the peroxide, only takes place slowly and after prolonged boiling. If, in fact, to a given quantity of peroxide dissolved in the equivalent amount of potash, we add, all at once, an excess of oxalic acid (a little more than the three molecules required by equation 3), we obtain almost immediately the final decolouration of the liquor, and this latter on cooling deposits the osmyloxalate; however, it only gives a small quantity, and at the same time it deposits, first in the melted state and then solid, the greater portion of the peroxide used. If the whole is now re-heated, the osmyloxalate and the peroxide both re-dissolve; after boiling for an hour, a fresh cooling will give much more osmyloxalate and much less peroxide than in the former case. However, the complete disappearance of the peroxide and its integral transformation into osmyloxalate cannot be effected except after further prolonged boiling for several hours.

II. Preparation of Osmyloxalate of Potassium.—In consequence of the above observations, the following method should be used for the preparation of osmyloxalate of potassium:—

A known weight of peroxide of osmium (say, about 20 grms.) is placed in a two-litre flask with an aqueous solution of pure potash (15 grms. in 500 c.c. of distilled water) and an excess of crystallised oxalic acid (50 grms.), so that the potash, and especially the oxalic acid, may be in excess with regard to the relative quantities required by equation 3. The neck of the flask must be connected with a vertical condenser in such a manner as to prevent as far as possible any contact of the fumes of the peroxide with any organic substance; grinding with emery powder will do very well, or an indiarubber ligature round two tubes of slightly different diameters, one fitting well into the other; these being the condenser tube and the neck of the flask. Finally, at the upper end of the condenser a bulb-tube is attached in a similar manner; this tube contains a little potash solution to retain any fumes of the peroxide that might otherwise escape from the condenser.

The apparatus being thus fitted up, the contents of the flask are brought to boiling-point; besides carbonic acid, fumes of peroxide are given off which condense in the condenser and fall back into the flask in the fused state. The boiling is continued until the evolution of peroxide fumes ceases; this requires several hours (at least three hours with the quantities given above). During this time, the contents of the bulb-tube must be frequently renewed as the potash is transformed into carbonate by the carbonic acid given off, and therefore becomes less able to arrest the osmic fumes; the partial decolouration that takes place, passing from deep reddish brown to bright yellow, shows the time when this renewal should be made.

When no more fumes of peroxide condense, the boiling is stopped; further boiling would interfere with the reaction, especially in the presence of a large excess of oxalic acid, since products of reduction of the osmyloxalate would be formed.

The limpid solution in the flask is allowed to cool, and soon a considerable deposit of crystals of osmyloxalate of potassium appears. After complete cooling, the whole of the contents of the flask is decanted into a Büchner funnel, in which the crystalline deposit is rapidly freed from the mother-liquor by means of the filter-pump. It is then further dried by squeezing between filter-papers.

When carried out with the above-mentioned precautions, the operation is not dangerous, as the crystals can be collected without any inconvenience from the fumes of the peroxide. Further, the return is almost quantitative (38 grms. for 20 grms. of peroxide); as a rule, the quantity of the salt corresponds with the fumes of peroxide collected in the potash tubes, and this latter can be used in subsequent operations.

Finally, the osmyloxalate of potassium, being very slightly soluble in the cold, as well in solutions of the

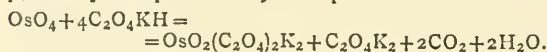
		Calculated.		Found.								
				I.	II.	III.	IV.	V.	VI.	VII.	Mean.	
Os		191.0	37.21	—	37.59	37.46	37.55	—	37.34	37.11	37.41	
2K		78.3	15.25	—	15.06	15.27	15.51	—	15.24	15.10	15.24	
4C		48.0	9.35	—	—	—	—	9.53	—	—	9.53	
10O		160.0	31.17	By difference							30.78	
2H ₂ O		36.0	7.02	6.93	—	7.19	7.02	—	7.03	—	7.04	
OsO ₂ (C ₂ O ₄) ₂ K ₂ ·2H ₂ O		513.3	100.00								100.00	

ordinary alkaline salts as in water, it is easily obtained in the presence of these salts; consequently, its preparation constitutes an excellent means for recovering, in the form of a stable and well-defined salt, the osmium from residues in which it is contained, so long as the metal is given off in the form of peroxide, although at the same time mixed with various acid fumes.

III. *Other Methods of Preparation.*—Besides the fundamental method of preparation which has just been described, two other methods may be used for obtaining osmyloxalate of potassium.

The first, the existence of which confirms one of the essential points of the theory already put forward, consists in the direct production of the second of the two reactions by which we explained the formation of the osmyloxalate from the peroxide. It suffices to make a concentrated solution of osmate of potassium, and to treat it while hot with an excess of oxalic acid, to obtain immediately, through the cooling of the mixture, an abundant deposit of osmyloxalate according to equation 2. The slight stability of aqueous solutions of osmate of potassium, which, especially when hot, become strongly impregnated with a black deposit of osmic acid, forms no obstacle to this operation; the deposit is re-dissolved, as has been seen above, in an excess of oxalic acid; however, these solutions can be made relatively stable by the addition of a small quantity of potash. In such a case the black precipitate of osmic acid will only appear transitorily during the course of the reaction, when the oxalic acid, added to the solution in the crystalline form, is still only partially dissolved.

We can also obtain the same salt by digesting peroxide of osmium with a concentrated solution of binoxalate of potassium. The mixture being made in the cold, and left in a ground stoppered flask, no reaction is observed at first, but after some months the solid peroxide disappears, and we find beautiful crystals of osmyloxalate of potassium at the bottom of the flask. The reaction which takes place may be represented by the equation:—



Though very slow in the cold, the reaction is accelerated by raising the temperature, but in the latter case more than in the former it is necessary to loosen the stopper occasionally to prevent the pressure of the carbonic acid, which is continually coming off, from becoming excessive. We may add that this method, though less practical than the preceding ones if quantities of osmyloxalate are required quickly, is, on the other hand, the only one by which crystals can be obtained sufficiently large for purposes of measurement with the goniometer.

IV. *Composition.*—The analysis of osmyloxalate of potassium offers special difficulties which do not occur in the case of the complex oxalates of the other metals of the platinum group; the ease with which finely divided osmium is oxidised on contact with the least trace of free oxygen, giving fumes of peroxide, necessitates the whole of the analytical operations being carried out in a current of hydrogen perfectly free from air.

As the method of procedure we adopted will be described shortly by one of us, we will restrict ourselves here to the results obtained.

The analyses I., II., III., IV., and V. were carried out on samples prepared by means of peroxide of osmium, oxalic acid, and potash; analysis VI. on a salt obtained

from the osmate, and number VII. on a salt prepared from peroxide and binoxalate of potassium.

Quite independently of proofs of a different kind which will be given later on, the analysis suffices to show that osmyloxalate of potassium is a hexavalent derivative of osmium, an osmyl salt comparable with osmysulphite of sodium, $\text{OsO}_2(\text{SO}_3\text{Na})_2\text{Na}_2$, recently described by Rosenheim and Sasserath (*Zeit. Anorg. Ch.*, vol. xxi., p. 124), and to the salts of osmyldiammonium, more especially the chloride, $\text{OsO}_2(\text{NH}_3)_4\text{Cl}_2$, the composition of which was elucidated in 1881 by Wolcott Gibbs (*Amer. Chem. Journ.*, vol. iii., p. 223).

V. *Properties.*—The crystallographic examination of osmyloxalate of potassium, which we owe to the kindness of H. Dufet, gave the following results:—

Triclinical crystals, formed of the facets, p (001), $f\frac{1}{2}$ (111); dominants, h_1 (100), g_1 (010), $d\frac{1}{2}$ (111), $b\frac{1}{2}$ (111), x (131), y (131).

The three latter are rare and small; the facets p and $d\frac{1}{2}$ are often imperfect.

Parameters .. $a:b:c::0.50044:1:1.05503$.

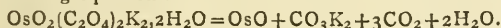
The optical sign is positive. One of the optical axes practically coincides with the normal to p (001). The plan of the axes makes an angle of 47° with the edge $pf\frac{1}{2}$ (001) (111), and of 77° with the edge pg_1 (001) (010). The angle of the axes, observed in air on the face p , is $64\frac{1}{2}^\circ$, the axis inclined to the normal is at the side of the angle $pf\frac{1}{2}$ (111) (010).

Dichroism is noticeable; in p the colour is greenish yellow for vibrations parallel to the plan of the axes, and yellowish brown for vibrations perpendicular to the plan of the axes.

The crystals of osmyloxalate, in the dry state are relatively very stable; when heated to about 80° they effloresce and lose their water of crystallisation without the anhydrous salt appearing to undergo the slightest decomposition, as well *in vacuo* and in air, as in hydrogen or carbonic acid. If they are heated more strongly, *in vacuo* to prevent the oxidising action of the air on the probable products of decomposition, it is not until a temperature of about 180° is reached that blackening is observed indicating the commencement of decomposition. This decomposition, which is complete when a dull red heat is reached, furnishes carbonic acid gas only; measurements of its volume show that three molecules of the gas are given off for one molecule of the salt (calculated, 25.7 for the hydrated salt; found, 27.2, 26.9, 27.2, 27.3, 27.1; mean, 27.1).

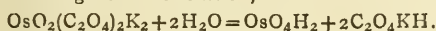
The black residue from this operation does not contain any metallic osmium, since when heated in a current of hydrogen it forms water-vapour; the collection and weighing of this water show that it is formed molecule for molecule of the salt (calculated, 3.51 for the hydrated salt; found, 3.74); consequently, the osmium in this residue exists in the form of the protoxide. The relative weight of this residue also corresponds closely to that required with regard to one molecule of the salt used, by the formula $\text{OsO} + \text{CO}_3\text{K}_2$ (calculated, 67.3 of the hydrated salt; found, 65.3, 65.5; mean, 65.4). Finally, this residue, either before or after reduction in hydrogen, has a strongly alkaline reaction, is very deliquescent, and effervesces with acids; it contains, therefore, an alkaline carbonate, which appears to be partially dissociated, as shown by the variations in the figures given above from the theoretical

figures. Consequently, the decomposition of the osmyloxalate of potassium by heat can be represented by the following equation:—



Osmyloxalate of potassium is very slightly soluble in cold water, but its solubility is notably increased as the temperature is raised. It is practically insoluble in water charged with chloride of potassium, even when warm.

Solutions thus obtained are very unstable; at about 80° they become cloudy, and give a black deposit of osmic acid, resulting from the reaction,—

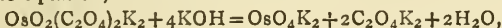


At the same time, the characteristic odour of peroxide of osmium is given off, the presence of which appears to be due to the rapid oxidising power of osmic acid in the presence of air and water, as shown by MM. Moraht and Wischin (*loc. cit.*, p. 156).

The same decomposition takes place in the cold, but much more slowly. It is prevented by the presence of a small quantity of oxalate of potassium, and more so by oxalic acid or a binoxalate, so the decomposition undergone by the salt on contact with pure water would be limited by the presence of the binoxalate formed. In the cold, the amount of oxalic acid necessary to give stability to a concentrated solution of osmyloxalate is very small, or c.c. of demi-normal oxalic acid solution is sufficient to prevent the decomposition of 100 c.c. of a saturated solution. But this amount must be increased if the solution to be made stable is to be heated; it may also be diminished with the dilution of the solution.

In the presence of a quantity of free oxalic acid sufficient to assure the stability of the solutions obtained, water dissolves about 0.75 per cent of its weight of the osmyloxalate at 15°, and 3 per cent at 50°.

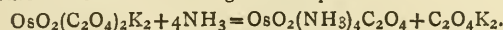
Different to oxalic acid, potash facilitates the decomposition of osmyloxalate of potassium; but the products of the reaction vary according to the manner in which it is effected. If we pour a slightly acid solution of osmyloxalate slowly into an excess of potash-lye, the mixture immediately takes the reddish violet tint of a solution of osmiate of potassium, and this salt, formed according to the equation,—



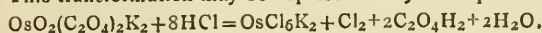
is deposited in the crystalline state on cooling, if sufficiently warm and concentrated solutions have been used.

If, on the other hand, the alkaline lye is added drop by drop to the solution of osmyloxalate, it will be seen that every drop will cause a deep brown colouration at the point where it touches the solution, similar to that which characterises the solutions of peroxide in potash. Even if the movement of the liquid prevents this local formation of colour, the tint of the whole becomes darker with the addition of increasing quantities of the alkali, and gradually tends towards black. At the same time a transitory, attenuated, black precipitate appears, which is formed apparently of osmic acid, and the characteristic odour of peroxide of osmium is also observed. But it is only when a large excess of alkali has been used that the violet tint of solutions of the osmiate is observed.

Ammonia, added in equal quantities to a solution of osmyloxalate of potassium, gives a yellow, crystalline precipitate; this is the oxalate of osmydiammonium, discovered in 1881 by Wolcott Gibbs (*loc. cit.*, p. 238) and which is formed according to the equation—



Hydrochloric acid, poured in excess over crystals of osmyloxalate of potassium, attacks them rapidly at about boiling-point, giving off chlorine and forming a yellow liquid, which on cooling deposits regular, deep red octahedra of chlorosmiate of potassium (Os calculated, 39.63—found, 40.09; 2KCl, calculated, 30.95—found, 30.37). This transformation may be represented by the equation



All these reactions which connect osmyloxalate of potassium with already known compounds of osmium, form so many indirect proofs of the formula to which the analysis of this salt brings us. Its transformation into osmic acid, or an osmiate by water or the alkalis, like its preparation from osmiate of potassium and oxalic acid, is effected without any evolution of gas; thus, there are no phenomena of oxidation or reduction in these reactions, and consequently the osmyloxalate is, like the osmiate, a hexavalent derivative of osmium. The change brought about by ammonia, and in which the group OsO_2 = characteristic of the osmyl salts is retained, leads to the same conclusion. Finally, its transformation into chlorosmiate, a salt derived from quadrivalent osmium, is accompanied by an evolution of chlorine, the estimation of which (calculated 13.8 per cent of the weight of the salt used,—found 14.1) verifies quantitatively the above equation, and thus furnishes a measurement of the difference in valency undergone by osmium in one salt and another.

The constitution of osmyloxalate of potassium being thus well established, it becomes possible to take it as the starting-point for the preparation of other osmyloxalates, and, more generally of other corresponding osmyl salts, like those of the type $\text{OsO}_2\text{X}_4\text{M}_2$.

This research, of which a few results have been already briefly published (L. Wintrebert, "On some Osmyloxalates"), will be the subject of a future paper.—*Bull. Soc. Chim.*, Series 3, vol. xxvii, No. 12.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1902.

By SIR WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M. Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, October 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 200 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 200 samples examined by us chemically during the month, all were found to be clear, bright, and well filtered.

Rain has only fallen on seven days at Oxford during the past month, the total fall being 1.11 inches, of which a considerable proportion, viz., 0.85 inch, fell on the 10th and 11th; the average rainfall for September is 2.39 inches. We have thus a deficit of 1.28 inches, which, added to the previous one of 5.35 inches, makes a total deficit for the year of 6.63 inches, or 36.6 per cent on the thirty-five years' average.

Our bacteriological examinations of 533 samples have given the results recorded in the following table; we have also examined 39 other samples, from special standpipes, wells, &c., making a total of 572 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	166
New River, filtered (mean of 128 samples) ..	14
Thames, unfiltered (mean of 26 samples) ..	2491
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 293 samples)	28
Ditto ditto highest	197
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	205
River Lea, from the East London Company's clear-water wells (mean of 34 samples) ..	20

Of the 455 samples taken daily from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, sixteen samples, or 3·5 per cent, were sterile. Two samples contained more than 150 microbes, while eighteen samples, or 3·9 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the eighteen excess samples was 128, against a corresponding mean of 142 in twelve samples during August, showing that the purity of the supply has improved during the month of September. In this respect the present autumn resembles those of the last few years in being exceptional in the purity of the River supply, owing to the extraordinarily diminished rainfall.

We are, Sir,

Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

OUR PRESENT KNOWLEDGE OF AROMATIC DIAZO-COMPOUNDS.*

By GILBERT THOMAS MORGAN, D.Sc., F.I.C.

(Continued from p. 191).

C. *Diazo-compounds Employed in the production of Azo-colouring Matters.*

1. *Aminoazo-compounds*.—The action of a diazonium salt on a primary aromatic amine gives rise either to a diazoamine or an aminoazo-compound, according as to whether the diazo-radicle remains attached to the aminic nitrogen or migrates into the aromatic nucleus. Aniline and its homologues and substitution products yield diazoamines, which are often capable of undergoing re-arrangement into aminoazo-compounds, this change being effected either by allowing the diazoamine to remain in alcoholic solution or by warming it with a mixture of the parent base and its hydrochloride. The latter mode of transformation has been studied quantitatively by Goldschmidt and his pupils (*Ber.*, 1896, xxix., 1369, 1899), with the following results:—

The transformation of diazoaminobenzene into aminoazobenzene in an aniline solution containing aniline hydrochloride is a monomolecular reaction, the velocity of transformation, in moderately dilute solution, being proportional to the temperature and to the amount of catalyst (aniline hydrochloride) but independent of the concentration. Benzenediazaminobenzene, when dissolved in aniline containing its hydrochloride, becomes converted into diazoaminobenzene and *p*-toluidine, the resulting diazoamine then undergoing transformation in accordance with the preceding rules.

This conversion takes place more slowly when the diazo-radicle shifts into the ortho-position with respect to the amino-group. The transformation constant of diazo-aminobenzene at 45° is 0.081, whereas the value of this coefficient for diazoamino-*p*-toluene is only 0.0095, the solutions employed in both cases being semimolar.

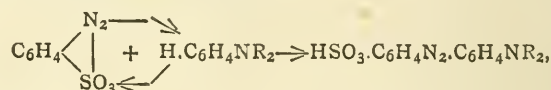
The existence of analogous intermediate diazoamino-compounds and diazohydroxy-derivatives in the commercial azo-colouring matters, has been recently demonstrated by Vaubel (*Zeit. Farben. Textilchem.*, 1902, i., 3).

Although aniline and other benzenoid primary amines give rise to diazoamines when treated with diazonium salts, their dialkyl derivatives containing a free para-position with respect to nitrogen, readily furnish azo-compounds of the methyl-orange type. The formation of these colouring matters is governed by the following laws (Goldschmidt and Merz, *Ber.*, 1897, xxx., 670 and 2075):—

(i.). The velocity of formation of the aminoazo-compound depends only on the nature of the reagents, and not on the concentration.

(ii.). In coupling the hydrochloride of a tertiary base with diazobenzene sulphonic acid, the interaction occurs between the diazo-compound and the base set free by the hydrolytic dissociation of its salt.

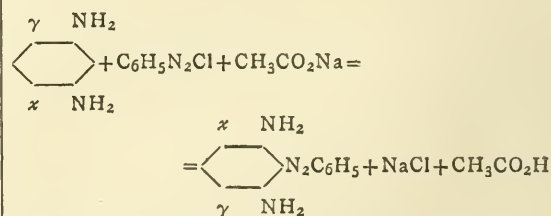
These laws are deduced from the following facts:—The concentration of the hydrochloride of the base or the diazo-compound, has no influence on the velocity of condensation. Excess of hydrochloric acid lessens the velocity. The formation of methyl-orange or the corresponding ethylated colouring matter,—



when carried out in the presence of different acids (e.g., acetic, mono-, di-, and tri-chloroacetic acids and hydrochloric acid), takes place most rapidly with the weakest acid, the velocity decreasing as the affinity constant of the acid increases.

Azo-derivatives of the aromatic *meta*-diamines, although amongst the oldest of the colouring matters, are still manufactured on a large scale for the use of the dyer. Bismarck brown, which was prepared even before the exact nature of the diazo-reaction had been elucidated, is still employed in the arts, and the precise composition of the commercial product has only recently been established by the researches of Täuber (*Ber.*, 1897, xxx., 2111, 2899; 1900, xxxiii., 2116).

Chrysoidine, first introduced by Witt (*Ber.*, 1877, x., 656), also maintains its position against the newer dye-stuffs. Its homologues and substitution products may be readily and quantitatively prepared from any of the derivatives of *m*-phenylenediamine, providing that these substances contain at least one free para-position with respect to an amino-radicle. If this condition is not fulfilled, the production of an azo-compound, although still possible if the diamine contains a free ortho position with respect to nitrogen, is nevertheless very considerably hindered. The formation of azo-derivatives from symmetrically disubstituted primary *m*-diamines has been demonstrated (Morgan, *Trans.*, 1902, lxxxi., 86), but the reaction—

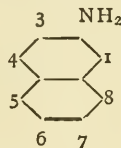


takes place with considerable difficulty, and the yield of azo-compound is small; moreover, the complete alkylation of the amino-radicles altogether prevents this condensation (*Trans.*, 1902, lxxxi, 650).

In the case of the naphthylamines and their sulphonic acids, the formation of ortho- and para-aminoazo-

* Report presented to Section B, British Association, Belfast Meeting, 1902.

compounds takes place with equal readiness; β -naphthylamine,—

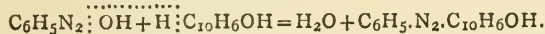


however, only yields azo-derivatives when the positions 1 and 8 are unoccupied. The presence of substituent radicles in either of these positions leads to the formation of diazoamines (Witt, *Ber.*, 1888, xxi., 3483; Morgan, *Trans.*, 1902, lxxxi., 91), and there appears to be no tendency for the diazo-group to migrate into position 3.

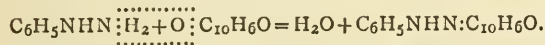
2. *Hydroxyazo-compounds*.—The formation of benzene-azophenol by the action of benzenediazonium chloride on an alkaline solution of phenol is a typical example of the method of preparing this important class of substances. Goldschmidt (*loc. cit.*) found that the essential reagents in this reaction are the diazo-hydroxide and the phenol set free by the hydrolysis of its alkali derivative. Excess of alkali hinders the condensation, the velocity of which diminishes as the concentration of the phenol or diazo-compound increases.

Although at first sight the mode of formation of hydroxyazo-compounds seems to leave little room for doubt as to the constitution of the products, yet this point has, for many years, been the subject of considerable controversy. This discussion arose from the fact that certain of these hydroxyazo-compounds can also be prepared by condensing the aromatic hydrazines with quinones; 4-benzene-azo- α -naphthol, for example, can be obtained either from benzenediazonium chloride and α -naphthol, or from phenylhydrazine and α -naphthoquinone. Similarly, the corresponding 2-benzene-azo- α -naphthol is produced either as a by-product in the former of these reactions, or by the action of phenylhydrazine on β -naphthoquinone, and the alternative methods of formation may be represented in the following manner:—

(i.). Azo-condensation,—

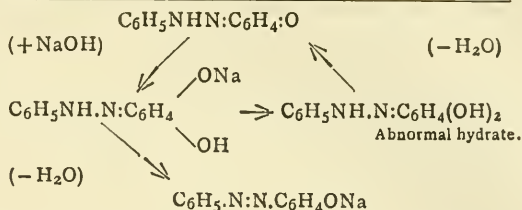


(ii.). Hydrazone condensation,—



Since the two reactions give rise to identically the same substance, it follows that intramolecular re-arrangement must have occurred during one or other or both of these condensations. This problem, which was for some years attacked by purely chemical methods (Liebermann, *Ber.*, 1883, xvi., 2858; Zincke, *Ber.*, 1884, xvii., 3026; 1887, xx., 3171; Meldola, *Trans.*, 1889, lv., 114, 603), has more recently been approached from the physico-chemical side, but even now the question can scarcely be said to be definitely settled. The cryoscopic determinations made by Auwers and his pupils (*Zeit. für Phys. Chem.*, xxi., 355, and *Ber.*, 1900, xxxiii., 1302) indicate that only the ortho-hydroxyazo-compounds are quinone-hydrazones the para-derivatives being phenolic. Chemical evidence in support of the azo-formula for the para-hydroxy-compounds is furnished by Hewitt (*Trans.*, 1900, lxxvii., 99, 712, 810), whilst Noelting's results show that these substances may also react as hydrazones (*Ber.*, 1887, xx., 2997).

The question has again been revived by Hantzsch, who places the hydroxyazo-compounds into the category of pseudo-acids. These are acidic substances which have a configuration differing from that of their salts, tautomeric change taking place during the formation of the metallic derivatives:—



The substance $\text{C}_6\text{H}_5\text{NHNH:C}_6\text{H}_4\text{:O}$ is a non-electrolyte, and hence its salt, when dissolved, should exhibit hydrolytic dissociation; this, however, is not the case, the metallic derivative behaving as the salt of a negatively substituted phenol. The hydrates of the azo-phenols, isolated by Hewitt (*Ber.*, 1895, xxviii., 799; 1898, xxxi., 2118), contain only half a molecule of water, but the compound $\text{Cl.C}_6\text{H}_4\text{NH.N:C}_6\text{H}_3\text{CH}_3(\text{OH})_2$ has been obtained (*Ber.*, 1899, xxxii., 3089), which corresponds with the abnormal hydrate required by Hantzsch's hypothesis.

The manufacture of hydroxyazo- and aminoazo-compounds has acquired considerable importance, owing to the fact that the products of the action of diazotised benzidine, tolidine, and *o*-dianisidine on the sulphonic acids of the naphthalenoid amines and phenols have the valuable property of dyeing un mordanted cotton—a quality which is also shared by the azo-derivatives of primulin and dehydrothio- β -tolidine, two amines containing sulphur which were discovered by Green (*Trans.*, 1889, lv., 227).

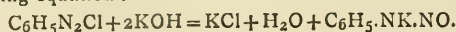
The sodium salt of sulphonated primulin can itself be dyed on cotton, and after being diazotised on the fibre and treated with a solution of a suitable phenol or amine, it gives rise to an insoluble azo-compound which, on account of the method of formation, is called an "ingrain" colouring matter.

These insoluble azo-compounds may also be produced by first impregnating a textile fabric with a phenol, and then treating the material with the solution of a diazonium salt. It was in the course of an investigation on diazo-compounds employed in the production of these "ingrain" azo-compounds that Schraube and Schmidt first isolated the so-called "isodiazo-compounds" (*Ber.*, 1894, xxvii., 520; Badische Anilin und Soda Fabrik, D.R.P. 78874, 80263, 81134, 81202). This important discovery inaugurated a new era of investigation on the diazo-compounds, and led to a revival of the discussion regarding their constitution—a question which had been in abeyance for many years.

II. THE CONSTITUTION OF DIAZO-COMPOUNDS.

A. Metallic Diazo-derivatives.

The alkali isodiazo-oxides, discovered by Schraube and Schmidt, are prepared by adding a solution of diazonium salt to a warm concentrated solution of an alkali hydroxide. The presence of negative radicles in the aromatic nucleus of the diazonium salt causes the transformation to take place more readily; the conversion of *p*-nitrobenzenediazonium chloride is effected, even at -10° , whilst the re-arrangement of the unsubstituted diazonium compound requires a very concentrated solution of alkali hydroxide, and a temperature of $130-140^\circ$. The more acidic diazo-compounds are transformed even by the action of the alkali carbonates (Schraube and Schmidt, and Badische Anilin und Soda Fabrik, *loc. cit.*). It was at first supposed that these isodiazo-oxides were metallic derivatives of the primary aromatic nitrosamines, the transformation taking place in accordance with the following equation:—



This view derived support from the fact that these metallic derivatives showed little or no tendency to yield azo-compounds with alkaline solutions of the phenols

moreover, they yielded nitrosamines of the secondary amines on alkylation.



That the nitrosamine formula is insufficient to account for all the reactions of the *isodiazio*-oxides was soon shown by von Pechmann, who obtained an oxygen ether, $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{OCH}_3$, from silver *iso*- β -nitrobenzenediazo-oxide; this methyl derivative has the properties of a diazonium salt, yields azo-compounds with the phenols and a diazoamine with aniline, and it evolves nitrogen on boiling with water, β -nitrophenol being simultaneously produced. It therefore follows that the hydroxide corresponding with these metallic derivatives exhibits the phenomenon of tautomerism. On neutralising a suspension of potassium *iso* β nitrobenzenediazo-oxide with a weak acid, a yellow substance is produced, which at first shows little tendency to form azo-compounds with β -naphthol, or its disulphonic acid, but when left in contact with dilute mineral acid, the product slowly dissolves and the soluble compound obtained has all the properties of the original diazonium salt. This change may be indicated in the following manner:—



This restoration of the capacity for coupling with phenols after acidification was at first considered to be characteristic of *isodiazio*-derivatives; but the test is not very decisive, since the metallic *isodiazio*-oxides themselves couple with β -naphthol dissolved in alkali hydroxide, providing that the solution is not too alkaline.

It was next found that potassium benzenediazo-oxide exists in two modifications, the *iso*-form previously mentioned and the normal form, which coupled with the phenols much more readily than its isomeride. This type of isomerism obtains generally amongst the metallic diazo-oxides, but the presence of negative substituents in the aromatic nucleus greatly diminishes the stability of the normal modification. On this account it is usually very difficult to obtain both isomerides in a state of purity.

Isomeric salts have, however, been prepared from diazobenzene sulphonic acid; the normal basic sodium salt, $\text{NaON}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}_4\text{H}_2\text{O}$, is obtained by working with cooled solutions, whilst the *iso*-salt, which separates in anhydrous crystals, is produced by heating a solution of its isomeride; they are both strongly alkaline, and are distinguished by their behaviour towards β -naphthol, the former salt readily coupling whilst the latter exhibits this property to a very slight extent. The corresponding potassium compounds have been isolated, and similar pairs of isomeric alkali salts have also been prepared from β -bromodiazobenzene-*o*-sulphonic acid (Hantzsch, *Ber.*, 1895, xxviii., 2002; 1900, xxxiii., 2158; and Gerilowski, *ibid.*, 2317).

Diazo- and Isodiazio oxides.—When the isomeric diazo-oxides were first investigated there existed a tendency to exaggerate the differences between the isomerides, and they were originally supposed to differ essentially in the following respects:—

- (i.). Capacity for coupling with phenols or ethyl acetoacetate and similarly constituted compounds.
- (ii.). Behaviour towards alkylating, reducing, and oxidising agents.
- (iii.). Interaction with benzoyl chloride and alkali hydroxides.

Production of Azo-derivatives.—The normal diazo-oxides exhibit the greater tendency to combine with the phenols, but in the case of both isomerides the rate of formation of hydroxyazo-compounds is largely dependent on the nature of the aromatic radicle attached to the diazo-group, and the free isomeric diazo-hydroxides couple with phenols even more readily than their potassium derivatives (Bamberger, *Ber.*, 1898, xxviii., 444).

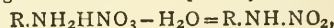
It was at first supposed that the metallic *isodiazio*-oxides did not condense with ethyl acetoacetate

(Schraube and Schmidt, *loc. cit.*), differing essentially in this respect from the normal derivatives which had long been known to furnish condensation products with the ester (Japp and Klingemann, *Ber.*, 1887, xx., 3398; *Annalen*, ccxlvii., 190; and Clarisen and Beyer, *Ber.*, 1888, xxi., 1697), but Bülow subsequently showed that the *isodiazio*-compounds yield mixed aliphatic-aromatic hydrazones or azo-derivatives (*Ber.*, 1898, xxxi., 3122; 1899, xxxii., 197). This correction, although suggesting the structural identity of the normal and *isodiazio*-oxides, does not assist in deciding between the two formulæ $\text{R}\cdot\text{N}:\text{NOH}$ and $\text{R}\cdot\text{NH}\cdot\text{NO}$, owing to the uncertainty which still exists with regard to the constitution of the aromatic and mixed condensation products, these substances being regarded by some authorities as azo-derivatives, and by others as hydrazones.

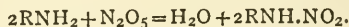
Alkyl Diazo-oxides.—The action of methyl iodide on the metallic *isodiazio*-oxides indicates that the *isodiazio*-hydroxide itself is a tautomeric substance, for the potassium salt yields a nitrosamine $\text{R}\cdot\text{NCH}_3\text{NO}$, whilst the silver derivative gives rise to an *O*-ether, $\text{RN}:\text{NOMe}$, this substance being also produced from the silver derivative of the normal diazo-hydroxide. This result indicates that the isomeric diazo-hydroxides corresponding with the two silver derivatives both have the same structural formula, $\text{R}\cdot\text{N}:\text{NOH}$. These *O*-ethers contain the diazo-radicle $\text{N}:\text{N}$, for they are all explosive and readily couple with the phenols in alkaline solutions (Bamberger, *Ber.*, 1895, xxviii., 225).

Reduction of the Metallic Diazo-oxides.—The members of both series, when treated with sodium amalgam, yield the corresponding hydrazines, provided that the reaction takes place in excess of alkali hydroxide (Hantzsch, *Ber.*, 1898, xxxi., 340).

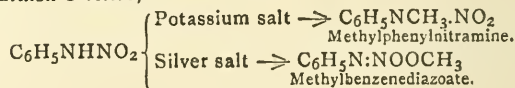
Oxidation of the Metallic Diazo-oxides; the Aromatic Diazoic Acids.—Even before the discovery of the *isodiazio*-compounds Bamberger had prepared acidic substances by the oxidation of the diazonium salts in alkaline solutions, and on repeating the experiment with the alkali *isodiazio*-oxides he obtained a larger yield of the oxidation product (*Ber.*, 1894, xxvii., 914). These acidic substances, the aromatic diazoic acids, are also obtained either by dehydrating the nitrates of the primary aromatic amines,—



or by the direct action of nitric anhydride on these bases,—



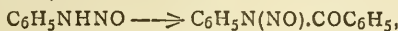
They readily undergo molecular re-arrangement, yielding nitro-amines, the nitroxyl radicles entering the nucleus either in the ortho- or para-position with respect to the aminic nitrogen (Bamberger, *Ber.*, 1893, xxvi., 471; 1894, xxvii., 359, 584, 2601). These properties indicate that the diazoic acids are nitramines; nevertheless they behave as tautomeric substances, for whereas their alkali salts give rise to secondary nitramines, their silver derivatives furnish *O*-esters,—



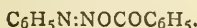
The methyl *O*-ester, when boiled with a benzene solution of β -naphthol, yields benzene-azo- β -naphthol, this condensation indicating its relationship to the diazo-compounds.

The Isomeric Diazo-oxides and the Schotten-Beaumann Reaction.—The normal and *isodiazio*-oxides, when treated with benzoyl chloride, yield nitrosobenzanilide with equal readiness, provided that the reaction is performed in the presence of a large excess of alkali hydroxide. The amount of benzoyl derivative produced is very small when the mixture is only slightly alkaline, the diminution in yield being greatest in the case of the normal isomeride (Hantzsch, *Ber.*, 1897, xxx., 621). This reaction, at first

sight, seems to favour the nitrosamine formula for the diazo-oxides,—

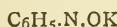


but von Pechmann's experiments (*Ber.*, 1892, xxv., 3199) indicate that the product is a tautomeric substance behaving also as if it had the formula—



Thus, when condensed with sodium β -naphthoxide, it yields benzeneazo- β -naphthol, and on treatment with cold potassium hydroxide solution undergoes hydrolysis, giving rise to potassium benzenediazo-oxide, a certain amount of this salt being also formed during the benzylation of the isodiazo-oxide.

Blomstrand, who advocated the diazonium formula—



N

for the normal diazo-oxide (*Journ. Prakt. Chem.*, 1896, liv., 329), supposed that the production of nitrosobenzanilide is due to the transformation of the benzoate—



N

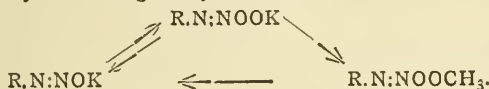
this, however, is not the case, for the ester when prepared from benzenediazonium chloride and silver benzoate does not yield any trace of nitroso-compound under similar experimental conditions (see also Bamberger, *Ber.*, 1897, xxx., 366).

Synthesis of Isodiazo-oxides.—The oxime formula for the metallic isodiazo-oxides also derives support from the fact that the alkali benzene-isodiazo oxide is produced by the action of hydroxylamine on nitrosobenzene in alkaline solutions,—



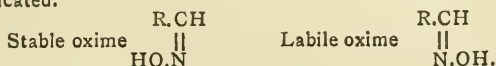
(Bamberger, *Ber.*, 1895, xxviii., 1218).

Since the isodiazo-oxide may be oxidised to the corresponding benzenediazoate, and reproduced from this substance or its alkyl ester by reduction with sodium amalgam, the cycle of changes may be thus indicated.

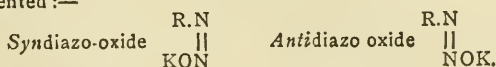


B. Stereo-chemical Relationship of the Isomeric Diazo-oxides.

The behaviour of the isomeric alkali diazo-oxides in the reactions described in the preceding section justifies the belief that the two series are structurally identical, and that the comparatively slight differences between the diazo- and isodiazo-derivatives are due to a different spatial arrangement of the radicles associated with the diazo-group, $\text{N}=\text{N}$. Accordingly, Hantzsch suggested that this isomerism is comparable with that which obtains among the oximes, the latter kind of isomerism being explained by supposing that the labile and stable modifications contain the associated radicles differently arranged about the complex $\text{N}=\text{CH}$ in the manner indicated.



The corresponding diazo-oxides would be thus represented:—



(Normal series.) (Iso series).

The assumption involved in both cases is the same—namely, that the third affinity of doubly linked trivalent nitrogen may be exerted in one or other of two definite

directions. If this be granted, then there can be little doubt that the labile normal diazo-oxides possess the *Syn*-configuration, for in this series the coalescence of the contiguous associated radicles readily occurs with the elimination of nitrogen. The stable isodiazo-derivatives should by exclusion have the *Anti*-structure (Hantzsch, *Ber.*, 1894, xxvii., 1702; 1895, xxviii., 676, 1734).

There is one point, however, in which the analogy between oximes and diazo-oxides breaks down; the stereo-isomeric oximes give rise to isomeric oxygen-ethers, whereas both the isomeric diazo-oxides yield the same *O*-ether. These *O*-ethers are explosive, and combine with bases and phenols in the presence of alkali hydroxides or carbonates yielding azo-compounds. They are accordingly placed by Bamberger in the *Syn* or normal series (*Ber.*, 1895, xxviii., 225). Hantzsch, on the contrary, points out that in their capacity for forming azo-derivatives they do not differ markedly from the *iso*- or *anti*-diazo-derivatives. The exact relationship of these ethers to the metallic diazo-oxides can scarcely be considered as finally settled.

The *iso*- or *anti*-diazo-oxides undoubtedly exhibit the phenomenon of tautomerism, and under certain conditions, react in accordance with the formula R.NH.NO , the formation of *N*-ethers, RN(alk).NO (secondary aromatic nitrosamines), being a case in point.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY OF NEW SOUTH WALES.

THE General Monthly Meeting of the Society was held at the Society's House, No. 5, Elizabeth Street North, on Wednesday evening, September 3, 1902; Prof. WARREN, M.Inst.C.E., Wh.Sc., President, in the Chair.

The following papers were read:—

"*Meteoric Dusts, New South Wales.*" By Professor LIVERSIDGE, M.A., LL.D., F.R.S.

The term meteoric dust is used because it is commonly applied to the materials forming the subject of this paper; it is not intended to state that the dusts are necessarily of cosmic or extra terrestrial origin. The specimens described and exhibited were from Moruya (fell on Dec. 15, 1880); from Uralla (fell on Dec. 14th, 1882); from near Broken Hill (fell 1896); from Menindie (fell June 17th, 1899); and Pambula (fell Oct. 5th, 1899). Dust from the roof-beams and mud from a covered cistern at the University and from the roof of the Observatory, Sydney; all three were collected in 1882. All the dusts are of a reddish colour except those from the University and Observatory, which are grey. The red dusts are mainly siliceous and argillaceous, and look as if they had come from dried-up water-holes; they contain a variety of organic and mineral matters such as might be expected from such a source, and in addition magnetite and metallic iron; the latter contains cobalt and nickel, which seems to indicate that, the dusts contain some cosmic or extra-terrestrial materials, part of which may have settled down and become mingled with the undoubted superficial terrestrial deposits and part may have been derived directly from the atmosphere. The University and Observatory dusts also yielded magnetite and metallic iron containing cobalt and nickel, and the University dust yielded particles of gold; the Observatory dust has yet to be tested. The Moruya, Menindie, and Barrier red dusts yielded particles of gold; the others have yet to be examined. Fuller information is given in the paper as to the constituents and chemical composition of the dusts, and analyses of volcanic and other dusts for comparison.

Gold in Meteorites.—Prof. LIVERSIDGE also exhibited under the microscope particles of a malleable yellow metal, which have all the appearance of gold, obtained

from certain Australian and European meteorites (siderolites). The presence of gold in meteorites bears upon the presence of gold in "meteoric" dusts, and it is also of great interest in connection with the presence of gold upon the earth and in sea-water, inasmuch as meteorites and the dust of meteorites are constantly falling upon the earth, to the extent of probably many million tons a year. Further information upon the question of the presence of gold in meteorites will be given shortly in a subsequent paper.

"A Rapid Method of Estimating Lime." By F. B. GUTHRIE, F.I.C., F.C.S., and C. R. BARKER.

The method consists of mixing previously dried and powdered ammonium nitrate with the calcium oxalate precipitate obtained in the usual manner. The oxalate is converted into calcium nitrate, which is very readily and completely converted to oxide by a few minutes' ignition over a Bunsen burner. Prolonged ignition over the blow-pipe is quite unnecessary, and effects no further alteration of the weight of the precipitate. Figures were given showing the accuracy of the method.

NOTICES OF BOOKS.

Inorganic Chemistry, with the Elements of Physical and Theoretical Chemistry. By J. I. D. HINDS. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1902. 8vo., pp. vii.—566, 69 illustrations, cloth.

In the preparation of this volume the author has undertaken to produce "a rather complete text-book on inorganic chemistry for colleges and universities, as well as a handy reference book for all students and teachers of chemistry"; and he "had in mind first an orderly and systematic treatment of the subject without reference to any teaching method."

These ideas have been successfully carried out by Prof. Hinds in this well printed volume, the matter of which is divided into four parts. Part I. contains a general introduction and a statement of its logical divisions; Part II. contains an outline of physical chemistry; Part III. treats more fully of theoretical chemistry; and Part IV. of descriptive chemistry. In classification and treatment the periodic system has been closely followed. A laboratory handbook to accompany this volume is in preparation.

In attempting to give the volume an encyclopædic character the author has enumerated many compounds with very little information concerning each; thus, at page 247, twelve halides and oxyhalides of tungsten are discussed in exactly thirteen lines, and the molybdenum halides at pages 243 and 244 fare little better. At the same time, justice is done to many of the rarer elements, as, for example, the "heliods." Some of the terms employed have an unfamiliar sound, such as vanadoids, scandoids, potassoids, &c.

The reviewer notes that throughout the work the author uses the spelling of chemical terms recommended by the Committee of the American Association for the Advancement of Science—chlorin, bromid, sulfur, &c.

The modern important theories advanced by Arrhenius, Ostwald, van't Hoff, and others are not mentioned in Parts II. or III.; bare reference is made to ionisation at page 97.

The volume can be commended for its very full treatment of the subject in a clear, systematic, and elementary manner. H. C. B.

Subject-list of Works on the Textile Industries and Wearing Apparel, in the Library of the Patent Office. London: Darling and Son, Ltd., and the Patent Office. 1902. Pp. 127.

THIS subject-list, which is marked No. 10, of the Patent Office Library Series, is arranged on the same general

plan as the preceding ones already noticed in this column; besides the subjects mentioned in the title, this list also includes works on the culture and chemical technology of textile fibres; the total number of works catalogued is 1138, being 1070 text-books and 68 serials, representing some 1896 volumes in all. The catalogue entries relating to these works number 1513, and are distributed under 185 headings and sub-headings.

Trades' Waste; its Treatment and Utilisation. With Special Reference to the Prevention of Rivers Pollution. A Handbook for Borough Engineers, Surveyors, Architects, and Analysts. By W. NAYLOR, F.C.S., A.M.Inst.C.E. With 21 Plates, 27 Folding Diagrams, and numerous Illustrations in the Text. London: Charles Griffin and Co., Ltd. 1902. Pp. 267.

THE causes and prevention of the pollution of rivers by trades' waste form the principal subject of this volume; the utilisation of trades' waste, except where rivers pollution is concerned, is only touched upon. The fact that the subject is receiving so much attention just now at the hands of engineers, chemists, and bacteriologists must not be attributed to any sudden increase either in the extent or degree of contamination to which rivers have all along been subjected, but rather to a more systematic endeavour to prevent such pollution, so that the rivers may safely serve as a source of domestic water supply to the towns situated along their course.

Sewage is by no means the only source of contamination to which rivers are subjected; woollen mills are great offenders, and as the water arrives at any point where the conditions for erecting a woollen mill are favourable, so does the character of the water commence to deteriorate unless proper preventive measures are taken.

In the *Journal of the Society of Chemical Industry* the various industries are divided into twenty-two classes, of which only five may be said to have no liquid waste of any consequence as to volume, while the remaining seventeen have both liquid and solid wastes, in most cases the liquid predominating. In some cases the provision of settling tanks is sufficient, but it often happens that the deleterious matter is in solution, and must be removed by precipitation and settling, local circumstances deciding all details.

The special trades dealt with by the author in this book are woollen mills, tanning and fellmongering, brewing and distilling, calico-bleaching, printing, and dyeing, paper making, and general chemical waste; these are all taken seriatim, and the various methods of purification proposed and adopted are all fully described and illustrated. There is a good table of contents, and a small index.

The Potash Salts; their Production and Application to Agriculture, Industry, and Horticulture. By Dr. L. A. GROTH, C.E., M.R.I. With a Preface by SAMUEL RIDEAL, D.Sc., Lond. London: The Lombard Press, Ltd. 1902. Pp. 286.

THE deposits of potassium salts are practically limited to German territory, and the recent development in the production, manufacture, and use of these salts has led to the creation of an entirely new and important industry, which in Germany actually competes in success with the coal and iron industries.

In France about 2000 tons per annum of commercial potassium chloride are obtained by the evaporation of sea-water; in India about 20,000 tons of nitrate of potash are obtained annually, and about 1200 tons come from the mines at Kalusz in Galicia, the only potash mine outside Germany. Canada has also exported about 2000 barrels a year, but this quantity has recently fallen off to some extent. These sources, however, are insignificant when compared with the present supply of over 3,000,000 tons a year, for the most part obtained from the great deposits of potash salts occurring naturally at various places in

Germany, and known in general as the Stassfurt potash salts.

There are now twenty potash mines working in Germany, nineteen of which are situated in the northern part of the Hartz district.

It seems fairly certain that these deposits owe their origin to the evaporation of a sea or ocean, but the actual process seems rather obscure, especially as the thickness of the deposits in some places reaches 3000, whereas sea-water containing 3 per cent of solids, even if the depth of the sea had been 30,000 feet, could only have deposited a salt-bed of 450 feet in thickness.

Omitting consideration of the gypsum, anhydrite, and rock-salt, the minerals found in the deposits may be divided, according to their chemical composition and commercial use, into two groups: the potassium and the magnesium salts; in regard to origin they may be classed as primary and secondary salts, the latter including such as have arisen from the solution and re-precipitation of the older deposits. The primary salts are often coloured reddish, the secondary are lighter in colour and much more pure.

It is extremely difficult to distinguish the different minerals by inspection only, and for this purpose, as well as to arrive at the value of the different salts, it is absolutely necessary that chemical analysis go hand in hand with mining.

The crude potash salts, principally carnallite, are partly consumed directly or after pulverisation, while the remainder are transformed into refined and concentrated products as required by chemical industry and agriculture.

The application of potash salts in agriculture is a question of extreme importance. Of the three important classes of artificial fertilisers, viz., nitrates, phosphates, and potash, the two former are generally better understood and more extensively employed than the latter, but the demand for potash is growing steadily, and the consumption for agriculture alone has increased from 71,000 tons in 1890 to 255,000 tons in 1900, calculated in pure potash (K_2O).

A large proportion of the book is devoted to the consideration of agricultural matters, and numbers of experiments with artificial manures are described.

The latter portion of the volume deals with the mining question only; engines, boilers, pumps, rock-drills, compressors, &c., are all described and illustrated, and a good deal of attention is paid to the adoption of electrical machinery both over- and under-ground. Thus the important question of the "potash salts" is dealt with in a thorough manner, both scientifically and commercially, and the whole forms a volume of considerable interest.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxv., No. 13, September 29, 1902.

New Experiments on the Limit of Intensity of the Current from a Pile corresponding to the Manifestation of an Exterior Electrolytic Action apparent in a Voltmeter.—M. Berthelot.—The author determines the limits of intensity of the current from a pile corresponding to the appearance of an exterior electrolytic action. He determines these limits with two different voltmeters: one containing dilute sulphuric acid only, with Wollaston electrodes,—a voltmeter in which the production of a reaction continues visible, and there exists a minimum electromotive force of 1.5 to 1.6 volts; and the other containing the same dilute acid added to pyrogallol—a voltmeter in which the hydrogen alone is evolved in a con-

tinuous stream under the influence of a minimum electromotive force of about 0.8 volt. The author successively varies the following conditions:—External pressure, concentration of the acid, concentration of the added pyrogallol, and excess of the electromotive force of the pile over the minimum electromotive force necessary for a continuous electrolysis. The external resistance used to obtain the limit at which the electrolytic action ceases to be manifest was varied from very small values up to 1,000,000 ohms. This resistance being measured, and also the electromotive force, the intensity, i , can be calculated from known formulæ, and from this the weight of hydrogen, h , evolved per minute can be deduced. Tables are given of the results obtained.

Preparation and Properties of a New Silicide of Vanadium.—H. Moissan and M. Holt.—The authors obtain a new silicide of vanadium, V_2Si , still less fusible in the electric furnace than the silicide VSi_2 . Its composition, density, and colour, besides its action on hydrochloric acid, and its easy decomposition by fusing silicon, are enough to differentiate it sharply from the silicide VSi_2 . The experiments described are a means of establishing the fact that the laws which govern the equilibrium of solutions at ordinary temperatures are equally applicable to the reactions of the electric furnace which are produced between silicon, copper silicide, and vanadium carbide at their boiling-points.

Nitropyromucic Acid and its Ethylic Ether. Di-nitrofurfurane.—R. Marquis.—The use of the nitrating mixture consisting of fuming nitric acid and acetic anhydride having been very successful in the case of furfuran, the author applies it to two other compounds of the same series—ethyl pyromucate and furfural. The ether obtained in the first case consists of yellowish white crystals melting at 101° . These are rapidly decomposed by caustic alkalis, dissolving and giving a red solution which contains an alkaline nitrite. This substance can easily be saponified by heating it in sealed tubes with water to 180° , nitropyromucic acid being thus produced, which melts at 185° .

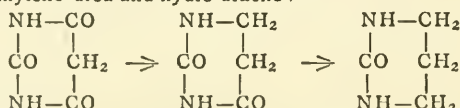
The Saponification of Nitric Ethers.—Léo Vignon and I. Bay.—The saponification of nitric ethers takes place according to particular rules. These rules are very complex, and they are determined just as well by the easy reduction of nitric acid, first to nitrous acid, then to free nitrogen, and finally to ammonia, as by the oxidation (varying in each case) of the alcohol obtained by saponification.

MISCELLANEOUS.

Monosalicylate of Glycerin.—E. Tauber.—In 1877 Göttig described as monosalicylate of glycerin a substance which he obtained by passing hydrochloric acid gas at 100° through a saturated solution of salicylic acid in glycerin; later on, he described this same substance as being a salicylic dichlorhydrine; this latter view is correct, but the author has observed that though by the action of hydrochloric acid in excess this dichlorhydrine is always obtained, it is sufficient if we wish to prepare the monosalicylate of glycerin, to react with only a small quantity of a mineral acid on a mixture of salicylic acid and glycerin in excess. By heating 100 grms. of salicylic acid, 300 grms. of glycerin, and 12 grms. of sulphuric acid diluted to 60 per cent of acid, for forty hours on the water-bath, the author obtained the ether in question, which, in the pure state, occurs in the form of white microscopic crystals, fusible at 76° . This ether is difficultly soluble in cold water, but easily so in warm water or alcohol; it is very easily saponified by the alkalis and their carbonates; it suffices to leave it in ethereal solution in contact with anhydrous carbonate of sodium or potassium to effect its saponification.—*Berichte*, vol. xxxiv., p. 1769.

Action of Iodine on Aconitine and Caffein.—C. Kippenberger.—It was thought formerly that the solution of iodine in iodide of potassium formed a periodide of constant composition with the salts of the alkaloids, according to the equation $\text{Alc. ClH} + \text{KI} + \text{I}_2 = \text{Alc. IH. I}_2 + \text{ClK}$. Previous experiments made by the author showed that this equation, as a rule, is inexact, and the present analyses confirm this idea. The practical consequences resulting from this are:—1. Aconitine and caffein cannot be estimated accurately in aqueous solution with an iodine solution, except by titrating this latter by comparison with aqueous solutions of these alkaloids. With caffein, it must be further seen that a notable proportion of the base remains in solution, or at least a large excess of iodine must be added. 2. The use of a solution of iodide of silver in iodide of potassium leads to the formation of a periodide of aconitine having almost exactly the composition $\text{C}_{34}\text{H}_{47}\text{NO}_{11}\cdot\text{HI. I}_2$. 3. The volumetric estimation of aconitine by saturation with a titrated acid in the presence of azolithmine, iodeosine, hematoxyline, or cochineal gives more exact results than titration with iodine.—*Zeit. Anal. Ch.*, vol. xxxix., p. 435.

Electrolytic Reduction of Barbituric Acid.—J. Tafel and A. Weinschenk.—The electrolytic reduction of barbituric acid (malonylurea) gives a mixture of trimethylene-urea and hydro-uracile:—



The barbituric acid was prepared by heating an alcoholic solution of urea and soda-malonic ether for a long time at boiling-point; the return was 45 per cent. The reduction was effected in solution in sulphuric acid at 50 per cent, and at about 18–20°. The sulphuric acid was precipitated with baryta, and the filtered liquid evaporated to dryness. The residue was exhausted with cold water, which leaves the hydro-uracile undissolved. This latter crystallises in warm water in flakes, fusible at 274°, subliming at a higher temperature, slightly soluble in the organic solvents, and easily soluble in the fixed alkalis. Hydro-uracile is not attacked either by permanganate of potash in sulphuric solution or by boiling hydrochloric acid. Cupro-ammoniacal solutions oxidise it when warmed. The mercuric derivative obtained by means of HgCl_2 in alkaline solution is crystalline and stable. The argentic derivative (also prepared in the presence of baryta) is in microscopic prisms, decomposed by warm water and by light. Hydro-uracile appears to be somewhat decomposed by boiling baryta. The trimethylene-urea remaining in the mother-liquor can be precipitated in the form of picrate in yellow needles, soluble in 35 parts of warm water; the sulphate occurs in cubical crystals.—*Berichte*, vol. xxxiii., p. 3383.

Analysis of Gutta-percha.—H. Borntrager.—The author has made the following determinations:—1. *Water*.—Desiccation of 2 grms. of material at 100°. 2. *Impurities*.—One grm. of the raw gutta-percha was treated with 50 c.c. of boiling benzene for twelve hours. This was passed through a tared filter and the residue weighed, after washing and drying at 110°. 3. *Pure Gutta-percha*.—The benzenic solution containing the gutta, the fluavil, and the albane, is concentrated to 50 c.c., and precipitated with 100 c.c. of absolute alcohol. After boiling for two hours it is filtered, and the residue dried at 100°, and weighed. 4. *Albane*.—The separate estimation of this substance not being of any technical importance, the sum of the fluavil and the albane is generally determined by difference. However, these two bodies can be separated by concentrating the benzenic solution, containing an excess of alcohol, down to 50 c.c. The albane, insoluble in alcohol, is precipitated on cooling; the decanted solution contains the fluavil. After evaporation and desiccation at 80°, these two bodies are

weighed. According to the author, albane is formed of three almost equal portions, of which the first two distil over at 200° and 250°.

Typical Analysis of a Raw Gutta-percha.

Water	1.5
Impurities	2.5
Pure gutta	77.5
Fluavil	6.0
Albane, a_1	3.8
" a_2	3.7
" a_3	5.0

—*Zeit. Anal. Ch.*, vol. xxxix., p. 502.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Revised Nomenclature.—Could any of your readers inform me if the reform chemical nomenclature mentioned in the *CHEMICAL NEWS* for June 10th, 1892, is generally adopted by the profession, or if not, what parts have been adopted?—C. ELLIOT.

MEETINGS FOR THE WEEK.

FRIDAY, 31st.—Physical, 5. "Existence of a Relationship between the Spectra of some Elements and the Squares of their Atomic Weights," by Dr. W. Marshall Watts. "The Size of Atoms," by H. V. Ridout. Exhibition of "Vacuum Calorimeters," by Prof. H. L. Callendar, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXXVI., No. 2240.

THE MICRO-STRUCTURE OF ZINC AND THE EFFECT OF SMALL AMOUNTS OF IMPURITY ON IT.

By ERNEST A. LEWIS, F.C.S.

THE structure of zinc containing small amounts of different metals, when studied microscopically, gives interesting results, as it shows the effect of small amounts of impurity on a pure metal very well.

In the following experiments chemically pure zinc was melted, along with 0.5 per cent of the various metals, except in the case of cadmium, arsenic, and phosphorus, which were dropped in the molten zinc; the crucibles were then allowed to cool down slowly.

Sections were cut from the centre of each and carefully polished and etched with very dilute nitric acid (1 part of strong nitric acid and 500 parts of water). The remainder of each alloy was re-melted at a low temperature and cast into small cast-iron moulds, and when cold, broken to compare the fracture with the microscopic structure.

No. 1.—Pure zinc consists of large primary crystalline grains, and inside the primary crystals, on deeper etching, are seen smaller secondary crystals. The fractured surface shows brilliant large bluish-white crystals.

No. 2.—Zinc containing 0.5 per cent of silver consists of small crystals of zinc surrounded by an eutectic alloy of silver and zinc. The fractured surface is finely crystalline.

No. 3.—Zinc containing 0.5 per cent of lead consists of both primary and secondary crystals. The primary crystals are similar to those of pure zinc, but the secondary crystals are surrounded by what is probably a solid solution of lead in zinc. The fractured surface is similar to pure zinc.

No. 4.—Zinc containing 0.5 per cent of copper is similar in structure to No. 2. It consists of crystals of zinc surrounded by an eutectic alloy of copper and zinc; the eutectic alloy is harder than the silver-zinc eutectic, as it shows up on polishing without etching. The fractured surface is finely crystalline.

No. 5.—Zinc containing 0.5 per cent of bismuth appears to consist of crystals of zinc surrounded by bismuth. The bismuth does not appear to alloy with zinc. The fractured surface is similar to pure zinc.

No. 6.—Zinc containing 0.5 per cent of cadmium consists of small crystals of a cadmium zinc alloy surrounded by zinc. The fractured surface is very finely crystalline.

No. 7.—Zinc containing 0.5 per cent of tin on very slightly etching shows up a network, but on deeper etching it is seen that the tin is part of each crystal; that is, the tin is thrown to the edges of the zinc crystals. The fractured surface is crystalline, but not so coarse as pure zinc.

No. 8.—Zinc containing 0.5 per cent of arsenic is similar to pure zinc. The fractured surface is crystalline.

No. 9.—Zinc containing 0.5 per cent of antimony consists of primary and secondary crystals. The primary crystals are similar to the crystals of pure zinc, but the secondary crystals are elongated and appear to be surrounded with antimony. The fractured surface shows large crystals similar to pure zinc.

No. 10.—Zinc containing 0.5 per cent of iron. The iron separates out in the crystalline form; it does not appear to form a true alloy with zinc. It probably is dissolved by molten zinc, and on cooling it is thrown out

again as crystals of iron. The fractured surface is fibrous.

No. 11.—Zinc containing 0.5 per cent of aluminium consists of small crystals of zinc surrounded by an eutectic alloy of aluminium and zinc. The fractured surface is very finely crystalline.

No. 12.—Zinc containing 0.5 per cent of manganese consists of primary and secondary crystals. The primary crystals are like those in pure zinc, but the secondary crystals are more elongated than those of pure zinc. The fractured surface is similar to pure zinc.

No. 13.—Zinc containing 0.5 per cent of nickel consists of small crystals of a nickel-zinc alloy surrounded by pure zinc. The fractured surface is finally crystalline.

No. 14.—Zinc containing 0.5 per cent of phosphorus is very similar to pure zinc, but the crystals are larger. Small quantities of phosphorus are soluble in zinc, without separating out. Phosphorus hardens zinc. The fractured surface is coarsely crystalline.

310, Dudley Road, Birmingham.

HISTORY OF THE COMMERCIAL MANUFACTURE OF ARTIFICIAL INDIGO.

By H. BRUNK.

THE manufacture of artificial colouring matters owes its existence to purely scientific researches, and its development is intimately connected with the progress realised by science.

The chemistry of artificial colouring materials has always been cultivated in the laboratories of the universities and of the higher schools, and the industry which has received the first gifts of science with enthusiasm follows the works of our great scientific men with sustained interest, in the hope of gathering the fruits of the rich harvest of their work.

But the young industry is no longer content with the gifts which come to it from scientific centres alone; many distinguished men have placed themselves entirely at its service. Such men as Caro, Glaser, Martius, and, later on, Laubenheimer, Duisberg, Bernthsen, and many others, have carried the spirit of scientific research into the domain of practical work. Henceforth, the industry will not be content with *receiving* only, it will also be able to *give*; it will carry out researches and enrich science.

Methods alone do not suffice commercially; processes are needed, and processes capable of being carried out practically. When the results obtained do not satisfy the exigencies of commerce, they must be put on one side, despite their eventual scientific value. Only that work the results of which have a practical value, and which can be effectively patented, is published to the world.

The result is that patents constitute almost the only source from which an idea can be formed of the results obtained from the chemical researches instituted with a practical object.

Unfortunately, patents only describe the results of a research, and do not give, like purely scientific publications, the successive steps which have been followed and those which have been abandoned; all that generally remains unknown. Such an example is indigo, the history of the development of whose manufacture is the task I am to-day confronted with.

The first complete synthesis of a vegetable colouring material was effected in 1868; Graebe and Liebermann pointed out the road which led from anthracene to alizarin, and industry took it up with magnificent success. The industry of the artificial colouring materials obtained a victory which gave it courage to direct its steps towards a still more difficult end—the conquest of the oldest and most important of the vegetable colouring materials, indigo.

The formation of indigo from orthonitroacetophenone was of no commercial use, but after his synthesis of indigo from isatin, completed by the synthesis of this latter substance, Ad. Baeyer, in 1880, effected his beautiful synthesis of indigo from orthonitrophenylpropionic acid. The problem of the manufacture of indigo then took a concrete form.

Orthonitrophenylpropionic acid was a derivative of cinnamic acid. This acid could be prepared from benzoic aldehyde by Perkin's reaction, and benzoic aldehyde again was easily prepared from toluene.

The Badische Anilin und Soda Fabrik and the Farbwerke vorm. Meister, Lucius, and Brüning acquired Baeyer's patents, and commenced, with the help of the inventor, the researches which lasted nearly twenty years, with the object of adapting the process to the requirements of industry.

They first succeeded in preparing cinnamic acid with chloride of benzyl and acetate of soda, instead of using Perkin's method. But from the commencement, orthonitrocinnamic acid was very expensive; the nitration of cinnamic acid by the usual methods only succeeded in transforming a small part of the acid into the orthonitrated derivative, while the greater portion was converted into a paranitrated derivative of no use at all in the manufacture of indigo. Eventually, by using cinnamic ether instead of the free acid, the nitration was effected in such a manner that 70 per cent of the acid was transformed into the orthonitrated derivative.

The bromisation of orthonitrocinnamic acid and the transformation of the bibromised acid into orthonitrophenylpropionic acid offered many practical difficulties, but the work carried out with energy and skill resulted, in the spring of 1881, in the manufacture of orthonitrophenylpropionic acid being carried out in a continuous manner. However, the process was not yet able to produce indigo at as low a price as the natural product, and the use of propionic acid was tried in another direction. At this time, indigo printing was the secret of a few houses only, and the idea occurred to effect the transformation of propionic acid into indigo on the fibre itself; this was successfully done when Caro found, in xanthogenate of soda, the appropriate means of reduction, but this success was theoretical rather than practical.

The year 1882 brought the synthesis of indigo by Baeyer and Drewson from orthonitrobenzoic aldehyde and acetone; it was much simpler than that from cinnamic acid, but the rational preparation of the orthonitrobenzoic aldehyde offered apparently insurmountable difficulties; only small quantities of this substance could be obtained by the direct nitration of benzoic aldehyde, together with a large quantity of the meta-nitrated derivative of no value for making indigo.

In 1886 the process of the direct oxidation of methylised benzenes into aldehydes was discovered, without previously transforming them into chlorised derivatives; this roused fresh hopes, and an attempt was made to produce orthonitrobenzoic aldehyde by oxidising orthonitrotoluene, but these experiments were unsatisfactory. Similarly to the process based on the use of propionic acid, the synthesis of indigo from orthonitrobenzoic aldehyde was able to be used partially in 1893, by Kalle and Co., who succeeded in obtaining the intermediate product of condensation, the orthonitrophenylacetic ketone, in the form of its easily soluble bisulphitic derivative. Several years then passed without anything further being published on this subject. It was only in 1896 that it became known that work in this field had been more active than ever.

The Farbwerke de Höchst had developed a commercial method for the transformation of orthonitrotoluene into orthonitrobenzoic aldehyde. This process consisted in treating the mixture of the chlorised products obtained from the chlorisation of orthonitrotoluene by aniline or sulphanilic acid, which transformed the chlorised orthonitrobenzyl into orthonitrobenzylaniline or the corresponding sulphonised acid. The product is transformed

by oxidation into the benzyldenic derivative, which, under the action of acids, splits up into orthonitrobenzoic aldehyde or aniline and sulphanilic acid.

At the same time the method of preparing orthonitrobenzoic aldehyde by the direct oxidation of orthonitrotoluene was completed.

Now that the problem of making orthonitrobenzoic aldehyde commercially was solved, the prospects of making indigo from this substance took a more favourable aspect, inasmuch as, through the increasing consumption of paranitrotoluene, there had been for some time an overproduction of orthonitrotoluene as a by-product; still there was not enough to make indigo for general use; all efforts were therefore turned towards a synthesis from a raw material which could be obtained in sufficient quantity.

In 1890, Hermann announced that he had obtained indigo by fusing phenylglycol with caustic potash. This synthesis only required materials that were cheap and plentiful, viz., aniline, acetic acid, chlorine, and alkalis.

However, though the materials were cheap and abundant, the return was too low to make a commercial success. The other glycines, viz., tolylglycine, xylylglycine, &c., behaved in the same manner as phenylglycine. The glycines of the naphthylamines either gave no indigo or not enough to be of any value. Besides, the tint was found not to be equal to that of indigo itself, and did not satisfy the dyers.

However, Hermann had also found that the glycol of anthranilic acid, phenylglycol, orthocarbonic acid, gave indigo. This method was more satisfactory, and experiments soon showed that it was capable of improvement. But the technical realisation of this synthesis was surrounded by extraordinary difficulties, which sometimes seemed to be insurmountable, and which were only overcome by the efforts of men who joined chemical knowledge with great commercial experience. Happily such men were to be found, and after seven years of hard work they succeeded in solving the problem. This brings me to the development of the manufacture of indigo as now carried out by the Badische Anilin und Soda Fabrik.

Phenylglycol, orthocarbonic acid is obtained by the action of monochloroacetic acid on anthranilic acid. To prepare the latter, it was necessary at first to start from orthonitrotoluene. The orthonitrotoluene could be either oxidised into nitrobenzoic acid, and this reduced; or, on the other hand, the product of the reduction of orthonitrotoluene, — orthotoluidine, — oxidised into anthranilic acid, passing, for example, through the acetyl derivative. This method had the same drawbacks as the formation of indigo from orthonitrobenzoic aldehyde. But it did not stop the undertaking. A method was found by Hoogewerf and van Dorp, by which anthranilic acid could be obtained from phthalic acid.

It was Hofmann who, by his researches on the particular action of bromine in alkaline solution on the acids, gave the idea to the above-mentioned chemists. They succeeded in transforming the imide of phthalic acid into anthranilic acid by means of bromine in alkaline solution.

With phthalic acid as the raw material for the preparation of anthranilic acid, it was naphthalene that became the raw material for the synthesis of indigo. At one stroke the commercial manufacture of indigo was placed on a solid basis. From this moment I had the firm conviction that the method on which we were engaged would bring us to the desired end, which was the substitution of synthetical for natural indigo.

Naphthalene is a raw material for the manufacture of indigo, which can be obtained in practically unlimited quantities. I have calculated that there are 28,000 tons of naphthalene which, for want of other use, are converted annually into lamp-black, or left dissolved in the heavy mineral oils, but which can be isolated at a very cheap rate. This amount is more than sufficient for the manufacture of all the indigo used in the world.

We were also in possession of the best known method for the manufacture of phthalic acid, a process which

consists of oxidising naphthalene with chromic acid, and which was discovered by one of our chemists twenty years ago. But as the cost of this method was too high, it became necessary to find a cheaper means for the oxidation of naphthalene.

M. E. Sapper succeeded in devising an entirely new method for the preparation of phthalic acid; this consisted of heating naphthalene with concentrated sulphuric acid, and a long series of experiments was undertaken with a view of making this process practicable. It was found that the addition of mercury to the sulphuric acid increased the yield of phthalic acid to a satisfactory amount. It is true that chance—the corrosion of a socket containing mercury—was the cause of this discovery, but without this accident the discovery would not have been made. The essential point of the process was the necessity of using very large quantities of concentrated sulphuric acid, and the recovery of this acid, pushed to its furthest point, was one of the conditions of success. If we had effected the recovery of the sulphuric acid in lead chambers the new process would have had no advantages over that based on the use of chromic acid; but here we were able to take advantage of R. Knietzsch's method for the manufacture of sulphuric acid. The so-called contact method of making fuming sulphuric acid was brought to such perfection at our works that the formation of sulphuric anhydride by the direct union of the gases from the pyrites ovens with the atmospheric oxygen was more economical than the manufacture in lead chambers.

The manufacture of phthalic acid was thus intimately connected with the new method of making sulphuric acid, as this method makes possible the direct and cheap transformation of the sulphurous acid resulting from the oxidation of the naphthalene into concentrated sulphuric acid. It was thus that we made our process a closed cycle of operations. The atmospheric oxygen can be economically introduced into the naphthalene, and our new method for the manufacture of sulphuric acid became one of the foundations of the manufacture of indigo.

At the same time, we were still endeavouring to cheapen the manufacture of the other substances necessary for the synthesis of indigo.

As the production of the necessary quantity of chloroacetic acid, as well as the oxidation of the phthalimide into anthranilic acid, required large quantities of chlorine, we had to look for a cheap source of this oxidising agent. Already, for the present manufacture of indigo, it is necessary to chlorise nearly 2,000,000 kilos. of glacial acetic acid a year. Neither the Weldon nor the Deacon method suffices for this; the former being too costly and the latter giving too dilute a gas.

At about this time, the electrolytic manufacture of chlorine and of alkaline chlorates was attracting attention, so we looked about for the method most suitable for our wants, and eventually decided on the method brought out by the Elekron manufactory at Griesheim S/M, as being the best. Still the purity of the chlorine produced by this method left something to be desired; however, in our process of the liquefaction of the chlorine we found an excellent means for purifying this gas up to the desired point.

The manufacture of the chloroacetic acid was not without difficulties, but even this, complicated at first, was transformed into a relatively simple operation.

The manufacture of phthalimide, of anthranilic acid, and of phenylglycinothocarbonic acid itself—the mother-substance of indigo—were not so easy as had been foreseen, and long series of systematic experiments was necessary to determine the most favourable conditions for obtaining the maximum yield of pure acid.

One of the most difficult operations was the fusion on the large scale; that is to say, the transformation of the phenylglycinothocarbonic acid by fusion with an alkali into the leuco-derivative giving indigo under the action of the atmospheric oxygen.

The indigo which is deposited in the aqueous solution

of the product of the fusion under the action of the atmospheric air, is crystalline. In cases where extreme fineness of the product is required, as in fermentation vats, the indigo obtained is treated with sulphuric acid, the sulphate obtained is decomposed by water, and thus transformed into an extremely fine powder, which is known in commerce as "indigo S."

I have attempted to give the broad outlines of the history of a new manufacture, and there only remains to point out a few factors which will make the influence of this manufacture felt in other branches of industry, and will even affect the conditions and future of the natural product.

The advantages that synthetic indigo possesses over the natural product have often been discussed; the uniformity, the constant proportion of pure indigo in the artificial product, the total absence of all impurities, the facility with which it can be reduced to an extremely fine state of division, which makes it of great value to the dyer, are all great advantages which it possesses over vegetable indigo. It satisfies the dyer who, for want of exact methods of analysis, had to buy, not according to the intrinsic value, but according to outward signs which were often fallacious.

On account of its great purity, synthetic indigo gives purer shades than natural indigo, and dyeing with artificial indigo has become a most simple and easy matter, while formerly with the natural product it required the experience of long years of practice.

Such is the history of our artificial indigo. It is seen that the new industry is not an unexpected gift from heaven. To bring the solution of the problem to a satisfactory conclusion, it has been necessary for many long years to make use of the intelligence and zeal of a staff of educated men, and that at a time when success seemed by no means certain. The first conditions of the practical synthesis of indigo were furnished by the results of a long scientific research. All the methods of advanced technical skill were at our disposal, and, thanks to the knowledge, the zeal, the energy, and the spirit of duty which animated our chemists, we have been able to accomplish a work which will, we hope, mark a distinct era of progress in civilisation.—*Moniteur Scientifique*, Series 4, vol. xv., No. 711.

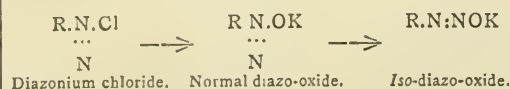
OUR PRESENT KNOWLEDGE OF AROMATIC DIAZO-COMPOUNDS.*

By GILBERT THOMAS MORGAN, D.Sc., F.I.C.

(Continued from p. 207).

B. Stereo-chemical Relationship of the Isomeric Diazo-oxides (continued).

Structural Formulae for the Isomeric Diazo-oxides.—The hypothesis that the isomeric diazo-oxides are structurally different has been defended by Bamberger (*Ber.*, 1895, xxviii., 444, 826, 1218) and Blomstrand (*Fourn. Prakt. Chem.*, 1896, liii., 169; 1897, liv., 305; 1897, lv., 480), who maintain that the normal diazo-oxide is a diazonium derivative, having the same configuration as the original diazonium salts. There is no longer any difference of opinion with respect to the oxime formula of the isodiazooxides, and accordingly the second hypothesis may be thus graphically illustrated—



One grave objection to the theory is at once detected

* Report presented to Section B, British Association, Belfast Meeting, 1902.

from this diagram, which indicates that the diazonium hydroxide—



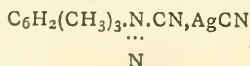
is capable of acting, not only as an acid, but also as a strong base. The difficulties attending this assumption will be considered at greater length in the sequel.

Existence of *Syn-diazo-Sulphonates, Cyanides, &c.*—Hantzsch, who obtained a very unstable red potassium benzenediazosulphonate isomeric with Fischer's yellow diazo-sulphonate, $\text{C}_6\text{H}_5\text{N}_2\text{SO}_3\text{K}$, asserted that these isomerides belonged to the *syn*- and *anti-diazo-series* respectively (*Ber.*, 1894, xxvii., 1726), but Bamberger objected to this classification, and showed that the red salt has the properties of a sulphite, $\text{C}_6\text{H}_5\text{N}_2\text{O.SO}_2\text{K}$ (*Ber.*, 1894, xxvii., 2930).

The former investigator has, however, succeeded in isolating a series of isomeric diazo-cyanides (*Ber.*, 1895, xxviii., 666). *p*-Chlorobenzenediazonium chloride, when treated with cold potassium cyanide solution, yields a labile salt which readily evolves nitrogen and forms *p*-chlorobenzonitrile on treatment with copper powder, and passes into a stable isomeride. The latter, which is not affected by copper powder and may even be distilled in steam, is undoubtedly the *anti-diazo-cyanide*, whilst the labile derivative belongs to the *syn-diazo-series*. Both isomerides have a yellow colour, and this fact tends to exclude the view that the labile derivative is a diazonium cyanide, for the diazonium radicle gives colourless salts with colourless acids.

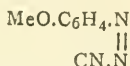
The *syn-diazo cyanides* are more stable when the aromatic nucleus attached to the diazo-group contains substituent radicles.

When a diazonium chloride is treated with a suspension of silver cyanide the colourless solution obtained, after filtering off the insoluble yellow *syn-diazo-cyanide*, contains a soluble double cyanide which is considered by Hantzsch and Danziger (*Ber.*, 1897, xxx., 2529) to be a diazonium derivative. The double cyanide derived from *p*-cumenediazonium chloride has been isolated and its properties are best expressed by the formula—

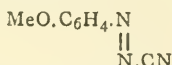


The *anti-diazo-cyanide* does not yield this double salt.

The formation of this double diazonium cyanide suggests that the sparingly soluble *syn-diazo-cyanide* may exist in solution in a state of equilibrium with the isomeric diazonium salt, and further confirmation of this hypothesis has recently been obtained (*Ber.*, 1900, xxxiii., 2161; 1901, xxxiv., 4166) by a study of the cyanides obtained from *p*-methoxybenzenediazonium bromide and chloride. These salts by double decomposition with potassium cyanide in alcoholic solution yield the *syn-diazo-cyanide*—



an orange-red insoluble substance (melting-point 51°) which couples with β -naphthol, and slowly changes into the non-coupling *anti-salt*—

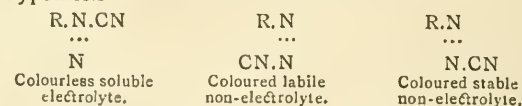


a brownish-red compound melting at 121° .

The existence of a third isomeric cyanide is indicated by evaporating at the ordinary temperature in the presence of excess of hydrogen cyanide an aqueous solution of *p*-methoxybenzenediazonium hydroxide. The colourless, crystalline substance obtained has the composition $\text{MeOC}_6\text{H}_4\text{N}_2\text{CN.HCN.2H}_2\text{O}$, and possesses all the properties of a true metallic salt; it is very soluble, and its solution is an electrolyte. Moreover, the double salt con-

denses with β -naphthol and is converted into the yellow *syn-diazo-cyanide* by the action of alkaline solutions.

These results show that diazotised *p*-anisidine gives rise to the three cyanides demanded by the stereochemical hypothesis—



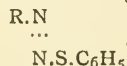
The opposite view only accounts for the existence of two isomeric cyanides, one having the constitution of a normal diazonium salt, and the other that of a diazo-cyanide of the *isodiazo-series*.

The *syn*- and *anti-diazo-cyanides* cannot be regarded as diazonium salts comparable with those of the mineral acids, for on the one hand they are non-electrolytes, dissolving only sparingly in water, and on the other they are distinctly coloured substances, readily soluble in the organic solvents.

Their colour confirms the assumption that they contain the group $\text{N}=\text{N}$, in common with azo-compounds. The criterion of colour must, however, be applied with caution, for the *syn*- and *anti-alkali salts* derived from diazotised sulphanilic acid are colourless.

Attempts made to obtain, in a state of purity, *syn*- and *anti-diazo-derivatives* containing other radicles in the place of cyanogen have not proved successful.

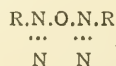
The diazonium salts or the alkali *anti-diazo-oxides*, when treated with the alkali phenylmercaptides, yield diazo-thioethers, which do not condense with β -naphthol, and are accordingly taken to belong to the *anti-series*—



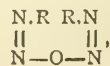
Only in the case of *p*-chlorobenzenediazothiophenyl ether was an explosive intermediate compound observed which may possibly be a *syn*-derivative. Phenol-*p*-diazo-hydroxide, $\text{HOC}_6\text{H}_4\text{N}_2\text{OH}$, and hydrogen sulphide yield a hydrosulphide, $\text{HOC}_6\text{H}_4\text{N}_2\text{SH.H}_2\text{S}$, which is possibly an *anti-diazo-derivative* (*Ber.*, 1895, xxviii., 3237).

By treating *p*-nitrobenzenediazonium chloride with hydrogen sulphide, Bamberger (*Ber.*, 1896, xxix., 272) obtained three products:—(i.) a hydrosulphide, $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{SH.H}_2\text{S}$ or $\text{NO}_2\text{C}_6\text{H}_4\text{N}(\text{SH}).\text{NH.SH}$, which, like the preceding thio-derivatives, does not couple with phenol; (ii.) a very explosive monosulphide, $(\text{NO}_2\text{C}_6\text{H}_4\text{N}_2)_2\text{S}$, condensing with phenols and decomposing in benzene at the ordinary temperature to yield *p*-nitrodiphenyl, hydrogen sulphide, and nitrogen; (iii.) a stable disulphide, $(\text{NO}_2\text{C}_6\text{H}_4\text{N}_2)_2\text{S}_2$, which slowly couples with the phenols, and is decomposed by benzene or toluene. The monosulphide is probably a *syn-diazo-derivative*, whilst the disulphide is considered to be an *iso-(anti)-diazo-compound*.

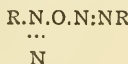
Diazo-anhydrides.—The isomeric alkali diazo-oxides differ in their behaviour towards cold dilute acetic acid, the *anti-diazo-oxides* giving rise to hydroxides $\text{R.N}_2\text{OH}$, which are colourless unless they contain substituent nitro-groups, whilst the *syn-isomerides* furnish extremely explosive yellow diazo-anhydrides (Bamberger, *Ber.*, 1896, xxix., 446). These substances, which may sometimes be obtained by treating a diazonium salt with an alkali *syn-diazo-oxide*, slowly couple with the phenols, yield *O*-diazo ethers with the alcohols, and react explosively with benzene, yielding diphenyl-derivatives. According to Bamberger's earlier papers the anhydrides should have the formula—



Hantzsch's stereo-chemical formula (*Ber.*, 1896, xxix., 1067),—

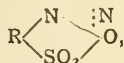


however, explains why the anhydrides readily yield *syn*-diazo-cyanides on treatment with hydrogen cyanide (*Ber.*, 1898, xxxi., 636), but only very slowly dissolve in hydrochloric acid to form diazonium chlorides. Bamberger has since suggested another formula for these substances, which assumes that they are salts of the basic diazonium hydroxide with the isomeric acidic diazo-hydroxide—

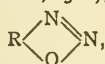


This configuration accounts for their formation from a diazonium chloride and an alkali diazo-oxide. The first of these formulae is the least probable, but it is not possible at present to decide between the remaining two.

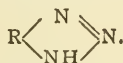
Cyclic-Diazo compounds.—Diazoised sulphanilic acid and other cyclic diazo-compounds are taken to be either diazonium salts,—



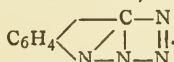
or *syn* diazo-anhydrides (Hantzsch, *Ber.*, 1895, xxviii., 1734; and *Ber.*, 1896, xxix., 1522),—



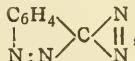
the introduction of negative substituent radicles increasing the tendency to assume the *syn*-configuration. The azimino-derivatives are assumed to be *syn*-compounds,—



The triazoles prepared by Bamberger (*Ber.*, 1899, xxxii., 1773) by the action of nitrous acid on amino-indazoles were assumed to have the formula,—

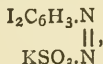


Hantzsch, however, advocates the constitution (*Ber.*, 1902, xxxv., 888)—

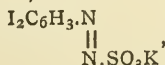


Diazo-sulphonates.—These substances, prepared by the action of potassium sulphite on the diazonium chlorides, appear generally to exist in two modifications, but in most cases the *syn*-isomeride is so unstable that it has not been isolated in a pure state. The fact that both modifications are distinctly coloured suggests that they have the constitution $\text{R.N:N.SO}_3\text{K}$, analogous to the azo-compounds; the *syn*-isomeride has invariably a more intense colour than the *anti*-salt.

Syn-2:4-di-iodobenzenediazo-sulphonate,—



is an orange substance, whilst the *anti*-salt,—



is yellow.

The naphthylamines behave exceptionally, yielding only *syn*-diazo-sulphonates; these are not converted into the *anti*-salt on warming, but decompose, yielding the corresponding azo-naphthalenes (Hantzsch and Schmidt, *Ber.*, 1897, xxx., 71).

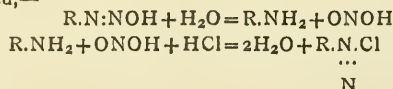
Diazo-phenylsulphones (Hantzsch and Singer, *Ber.*, 1897, xxx., 312).—By the action of benzenesulphonic acid on the diazo-cyanides, diazo-sulphones $\text{RN}_2.\text{SO}_2\text{C}_6\text{H}_5$ are produced; the action goes immediately with *syn*-diazo-cyanides, but only slowly with their *anti*-salts. The products do not exhibit stereo-isomerism, and probably belong to the *anti*-series; the *syn*-series has not been isolated.

C. Diazoamines considered as Anti-diazo-compounds.

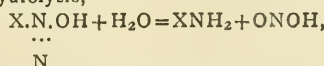
Isodiazotisation of Aromatic Primary Amines.—The action of nitrous acid on the salt of an aromatic amine leads to the production of a diazonium salt, the basic nitrogen atom retaining its pentavalency throughout the operation. When the interaction occurs between nitrous acid and the free base, an *iso*-diazo-hydroxide is formed which condenses with a molecular proportion of primary amine, yielding a diazoamine. The direct isodiazotisation of the base may also be effected either by passing nitrous fumes into its solution in dry ether or ethyl acetate (*Ber.*, 1894, xxvii., 1948), or by treating the amine with an alcoholic solution of amyl nitrite and sodium ethoxide (*Ber.*, 1900, xxxiii., 3511); in the former case a mixture of normal and *iso*-diazo-hydroxides results, whilst the latter experiment gives rise to the alkali *isodiaz*-oxide.

Migration of the Diazo radicle.—Griess noticed that a solution of diazobenzenesulphonic acid and *p*-toluidine hydrochloride gave the reactions of a mixture containing *p*-toluenediazonium chloride and sulphanilic acid (*Ber.*, 1882, xv., 2190), and more recently Schraube and Fritsch (*Ber.*, 1896, xxix., 287) showed that a similar rearrangement occurs in the case of a dilute solution of *p*-nitrobenzenediazonium chloride and *p*-toluidine. These investigators state that the direction of the change is constant either in acid or neutral solution; the velocity of migration, however, diminishes rapidly as the amount of acid is increased, and a large excess of this reagent altogether prevents the transformation. These results appear to show that the diazo-radicle passes from the less to the more positive radicle, but Hantzsch and F. M. Perkin found that a migration in the opposite sense occurs with benzenediazonium chloride and *p*-bromaniline (*Ber.*, 1897, xxx., 1412). It may therefore be supposed that generally, when neutral or slightly acid solutions of a diazonium salt and a primary aromatic amine are mixed, there will be a certain amount of rearrangement due to the migration of the diazo-group.

This migration of the diazo-radicle is probably associated with the changes which occur when this group passes from the diazonium to the diazo-configuration. Bamberger (*Ber.*, 1895, xxviii., 826) found that, in the inverse change, a transitory elimination of nitrous acid occurred,—



this reaction being effected by dissolving an alkali *iso*-diazo-oxide in cold mineral acid. If the transitory elimination of nitrous acid is assumed to occur in the change from the diazonium to the diazo-condition, then an explanation of the migration of the diazo-radicle is obtained, which also accounts for the fact that the same mixed diazoamine is produced from the couple XN_2Cl and YNH_2 as from the combination of YN_2Cl and XNH_2 . In the former case the diazonium hydroxide, liberated from its salt by the addition of sodium acetate, would undergo hydrolysis,—



and the nascent nitrous acid would at once isodiazotise a portion of each of the primary amines XNH_2 and YNH_2 , giving rise to the diazohydroxides X.N:NOH and Y.N:NOH . The latter substances and the unaltered primary bases would then condense, and a mixed diazoamine would be produced, this substance consisting of a solid solution of $\text{XN}_2.\text{NH}_2$ in $\text{YN}_2.\text{NHX}$, the proportion of the two constituents depending on the nature of the two aromatic radicles X and Y. In certain cases the product may consist largely of the symmetrical diazoamines $\text{XN}_2.\text{NHX}$ and $\text{YN}_2.\text{NH}_2$, but the formation of these compounds is equally well explained by the hypothesis based on the transitory elimination of nitrous acid. The

formation of the mixed diazamine occurs even when X and Y are radicles derived from different hydrocarbons, and substances of this type containing naphthalene and tetrahydronaphthalene nuclei have been isolated (Morgan, *Trans.*, 1902, lxxxi, 91; and C. Smith, *Trans.*, 1902, lxxxi, 901).

The migration of the diazo-group is prevented by the alkylation of the primary aromatic amine, and the couples XN_2Cl , YNHR and YN_2Cl , XNHR give rise to two isomeric mixed alkyl diazo-amines, XN_2NRY and YN_2NRX (Meldola and Streatfield, *Trans.*, 1887, li., 818; 1889, lv., 610, 1105; 1890, lvii., 785).

The comparative stability of the diazoamines and their production from isodiazo oxides point to their having the *anti* diazo configuration, the *syn*-isomerides have not been produced, although Hantzsch and F. M. Perkin (*loc. cit.*) obtained abnormal diazo-amines which form an exception to the rule governing the formation of mixed diazoamines. The compound $\text{ClC}_6\text{H}_4\text{N}_3\text{HC}_6\text{H}_5$, for example, exists in two modifications, which give rise to the same products on fission with hydrochloric acid or phenylcarbimide. The suggestion that these two isomerides should be represented by the formulæ $\text{C}_6\text{H}_5\text{N:N.NH.C}_6\text{H}_4\text{Cl}$ and $\text{C}_6\text{H}_5\text{.NH.N:NC}_6\text{H}_4\text{Cl}$, is not justified by the result of their fission.

(To be continued).

THE ESTIMATION OF BORIC ACID BY THE DIRECT ACTION OF ARSENIOS ACID.*

By F. A. GOOCH and J. C. BLAKE.

In a former paper from this laboratory (Gooch and Pulman, *Am. Journ. Sci.*, 1901, xii., p. 450), it has been shown that iodic acid may be reduced quantitatively by arsenious acid. In the work of which the present paper is an account the attempt has been made to apply arsenious acid similarly to the quantitative estimation of boric acid, according to the equation $3\text{H}_3\text{AsO}_3 + \text{HBrO}_3 = 3\text{H}_3\text{AsO}_4 + \text{HBr}$.

In the following series of experiments, made to discover the limits within which regularity of action might be expected, definite amounts of arsenious oxide dissolved in acid potassium carbonate were mixed with measured portions of a solution of potassium bromate, sulphuric acid was introduced in the amounts indicated, and, after standing either at the ordinary temperature, on the steam-bath or at the boiling temperature, potassium acid carbonate was added and the arseniate remaining was titrated with iodine to colour, the indication being confirmed by addition of starch. The conditions of acidity, the excess of arsenious oxide, the dilution, the time of action, and the temperature were varied within wide limits. The potassium bromate for this particular series of experiments was thrice re-crystallised from water, dried at 110° , and made up in solution containing 2.8 grms. to the litre. Of this solution 25 or 50 c.m.³ were measured out for each experiment.

An examination of these results discloses the fact that for conditions varying within a rather wide range the oxidation of the arsenious oxide reaches a fairly definite limit. The bromate effects practically the same proportionate oxidation of arsenious oxide in a volume of 200 c.m.³ or less, whether the sulphuric acid of half-strength present amounts to 3.5 c.m.³ or 10 c.m.³, and whether the time of digestion is fifteen minutes or thirty minutes at the boiling temperature one and one-half or four hours on the steam-bath, or two days at the ordinary temperature. Setting aside those experiments in which the addition of acid did not exceed the equivalent of alkali carbonate present by more than 1 c.m.³, the average

TABLE I.—Volume not Exceeding 200 c.m.³.

KBrO ₃ taken. Grm.	As ₂ O ₃ taken. Grm.	H ₂ SO ₄ (1:1) taken. C.m. ³ .	Time of digestion. Mins.	As ₂ O ₃ unchanged. Grm.	As ₂ O ₃ un-oxidised. Grm.	Error, in terms of KBrO ₃ . Grm.
<i>Heated at the Boiling Temperature.</i>						
0.1400	0.4950	10	30	0.2476	0.2474	0.0008—
0.1400	0.4950	10	30	0.2480	0.2470	0.0010—
0.2400	0.6188	10	20	0.3708	0.2480	0.0006—
0.1400	0.7425	8	25	0.4941	0.2484	0.0003—
0.1400	0.7425	8	25	0.4943	0.2482	0.0004—
0.1400	0.6188	7	20	0.3704	0.2484	0.0003—
0.1400	0.6203	7	20	0.3720	0.2483	0.0004—
0.1400	0.6188	5	15	0.3712	0.2476	0.0008—
0.1400	0.4950	3.5	15	0.2480	0.2470	0.0010—
0.1400	0.4950	3.5	15	0.2482	0.2468	0.0011—
0.1400	0.4950	2.5	15	0.2629	0.2321	0.0097—
0.0700	0.2475	5	15	0.1240	0.1235	0.0005—
0.0700	0.2475	5	15	0.1239	0.1236	0.0004—
0.0700	0.2475	5	15	0.1258	0.1217	0.0015—
0.0700	0.2475	5	15	0.1244	0.1231	0.0007—
0.0700	0.2475	5	10	0.1239	0.1236	0.0004—
0.0700	0.2475	5	10	0.1237	0.1238	0.0003—
0.0700	0.1584	5	10	0.0345	0.1239	0.0003—
0.0700	0.1584	5	10	0.0357	0.1227	0.0009—
0.0700	0.1584	5	10	0.0356	0.1228	0.0009—
0.0700	0.1584	5	10	0.0353	0.1231	0.0007—
0.0700	0.1881	5	10	0.0649	0.1232	0.0007—
0.0700	0.1881	5	10	0.0640	0.1241	0.0002—
0.0700	0.1881	5	10	0.0649	0.1232	0.0007—
0.0700	0.1881	5	5	0.0652	0.1229	0.0008—
0.0700	0.1881	5	5	0.0652	0.1219	0.0008—
0.0700	0.2475	2.5	10	0.1238	0.1237	0.0004—
0.0700	0.2475	2	10	0.1235	0.1240	0.0002—
0.0700	0.2475	1.15	10	0.1242	0.1233	0.0006—
0.0700	0.2475	1.15	10	0.1240	0.1235	0.0005—
0.0700	0.2475	1.15	5	0.1300	0.1175	0.0038—

Heated on the Steam-bath -80° .

0.1400	0.4950	10	150	0.2476	0.2474	0.0008—
0.1400	0.4950	10	150	0.2476	0.2474	0.0008—
0.1400	0.4950	4	240	0.2473	0.2477	0.0007—
0.1400	0.4950	4	240	0.2475	0.2475	0.0008—
0.1400	0.4950	4	180	0.2472	0.2478	0.0006—
0.1400	0.4950	4	180	0.2470	0.2480	0.0005—
0.1400	0.4950	3.5	90	0.2475	0.2475	0.0008—
0.1400	0.4950	3.5	90	0.2476	0.2474	0.0008—
0.0700	0.2475	1.15	30	0.1622	0.0853	0.0217—

Digested at the Ordinary Temperature.

			Hours.			
0.1400	0.4950	4	46	0.2480	0.2470	0.0005—
0.1400	0.4950	3.5	41	0.2475	0.2475	0.0008—
0.1400	0.4950	3.5	41	0.2470	0.2480	0.0005—
0.1400	0.4950	3.5	17	0.2490	0.2460	0.0016—
0.1400	0.4950	3.5	17	0.2492	0.2458	0.0017—

absolute variation from theory of the entire list of forty-two experiments amounts to 0.0007—grm. in terms of bromate, individual variations departing from the average by about the same figure. The obvious meaning of this fact seems to be that the slight error is due to impurity in the potassium bromate employed and not to incomplete oxidising action on the part of the bromate.

In the following series of experiments another preparation of bromate was employed, and its value was fixed by reduction with acidified potassium iodide and titration of the iodine set free according to the method formerly proposed by Kratchmer (*Zeit. Anal. Chem.*, 1885, xxiv., 546). The rate at which the action proceeds according to the equation $6\text{HI} + \text{HBrO}_3 = \text{HBr} + 3\text{H}_2\text{O} + \text{I}_2$, has been investigated by Ostwald (*Zeit. Phys. Chem.*, 1888, ii., 127), by Noyes (*Zeit. Phys. Chem.*, 1896, xix., 599), and by Judson and Walker (*Journ. Chem. Soc.*, 1898, lxxiii., 410). Time of action, proportion of iodide to

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, [4], xiv., No. 82.

TABLE II.

A.									
	KBrO ₃ taken. Grm.	= Iodine taken. Grm.	KI taken. Grm.	H ₂ SO ₄ (1 : 1). C.m. ³ .	Time of standing. Hours.	Approximate volume. C.m. ³ .	Iodine found. Grm.	Error, in terms of KBrO ₃ . Grm.	
1.	0.1410	0.6423	1	5	none	150	0.6223	0.0044 —	
2.	0.1410	0.6423	1	5	none	200	0.5929	0.0108 —	
3.	0.1400	0.6378	3	5	$\frac{1}{2}$	100	0.6343	0.0008 —	
4.	0.1400	0.6378	3	5	$\frac{1}{2}$	100	0.6329	0.0011 —	
5.	0.1400	0.6378	3	5	$\frac{1}{2}$	100	0.6329	0.0011 —	
6.	0.1408	0.6416	3	5	22	100	0.6366	0.0004 —	
7.	0.1408	0.6416	3	5	22	100	0.6364	0.0011 —	
8.	0.1408	0.6416	3	5	22	100	0.6381	0.0008 —	
9.	0.1400	0.6378	3	2.5	$\frac{1}{2}$	100	0.6340	0.0008 —	
10.	0.1400	0.6378	3	2.5	$\frac{1}{2}$	100	0.6336	0.0009 —	
11.	0.1400	0.6378	3	2.5	$\frac{1}{2}$	100	0.6336	0.0009 —	
12.	0.1400	0.6378	3	1	$\frac{1}{2}$	100	0.6343	0.0008 —	
13.	0.1400	0.6378	3	0.5	$\frac{1}{2}$	100	0.6331	0.0010 —	
B.									
	HCl (sp. gr. 1.18).								
14.	0.1400	0.6378	3	8	$\frac{1}{2}$	100	0.6336	0.0009 —	
15.	0.1400	0.6378	3	8	$\frac{1}{2}$	100	0.6329	0.0011 —	
16.	0.1400	0.6378	3	8	$\frac{1}{2}$	100	0.6336	0.0009 —	
17.	0.1400	0.6378	3	4	$\frac{1}{2}$	100	0.6336	0.0009 —	
18.	0.1400	0.6378	3	4	$\frac{1}{2}$	100	0.6333	0.0010 —	
19.	0.1400	0.6378	3	4	$\frac{1}{2}$	100	0.6340	0.0003 —	
20.	0.1400	0.6378	3	4	1	100	0.6336	0.0009 —	
21.	0.1400	0.6378	3	4	1	100	0.6333	0.0010 —	
22.	0.1400	0.6378	3	4	1	100	0.6336	0.0009 —	

bromate, excess of acid, and dilution are all, within limits, determining factors in the reaction; but in the analytical process it is usually assumed that the reaction goes soon to completion if free acid and a moderate excess of potassium iodide are present. In Table II. are recorded the results of experiments in which measured amounts of standard solutions of potassium bromate (approximately 2.8 grms. to the litre) were treated with potassium iodide and hydrochloric or sulphuric acid for definite times in glass-stoppered bottles, the iodine liberated being determined by titration with sodium thiosulphate standardised against nearly decinormal iodine of value fixed by comparison with decinormal arsenious oxide dissolved in acid potassium carbonate.

In Experiments 1 and 2 the excess of potassium iodide was only about 20 per cent over the amount demanded by theory, the time of standing was only the few minutes required for the manipulation of the process, and the dilution was considerable. It is obvious that under these conditions the reaction is very incomplete. On the other hand, a glance at the table makes it evident that the oxidation in all other experiments, whether in A or B, proceeds to practically the same point, showing similar errors. So it appears that the variation in the amount of acid above the minimum, the kind of acid (whether sulphuric or hydrochloric), and the time above the minimum half-hour, within the limits defined, are without apparent effect upon the reaction in the presence of the amount of potassium iodide used, approximately four times the amount required by theory. The balancing error due to the evolution of iodine by the action of atmospheric oxygen upon the acidified solution of the iodide was found by experiment to vary with the strength of the acid and the time of exposure, from 0.0001 grm. to 0.0003 grm. expressed in terms of the bromate, and these values are not greater than the differences observed between parallel determinations of the same sort. Probably, therefore, all the errors as shown in the table should really be increased a trifle to approximate the truth, notably those of the experiments allowed to stand the longest period, twenty-two hours.

The average apparent error of the process as applied to this particular sample of bromate is 0.0009— grm; and 2.5 c.m.³ of sulphuric acid of half-strength (1:1) or the

equivalent amount of hydrochloric acid, 4 c.m.³ of the acid of sp. gr. 1.18, in the presence of about 3 grms. of potassium iodide, complete the action within a half hour, at a dilution of 100 c.m.³, as far as it will go under any of the conditions tried. The phenomenon noted by Ostwald (*loc. cit.*, p. 131), that small amounts of hydrochloric acid tend to force the reaction more rapidly than equivalent amounts of sulphuric acid, does not appear in these experiments, no doubt because the action was pushed to the limit by the smallest amount of the weakest acid employed.

The error of deficiency shown again appears to be due to impurity in the sample of bromate rather than to incompleteness of the reaction. If the reaction were incomplete it would be natural to look for the cause in the possibility of the inhibiting influence of the iodine set free (Judson and Walker, *loc. cit.*, p. 411), but it was found in three parallel experiments that the introduction of 0.5 grm. of free iodine dissolved in potassium iodide failed to influence the error appreciably. For the present purpose, however, the absolute purity of the bromate is not a matter of moment, if, as seems to be the case, Kratchmer's reaction indicates its value with accuracy, as the basis of experimentation. It seems safe to assume, then, that the average result of Experiments 3 to 22 will give a very fair value for the sample of bromate investigated. That is to say, the experiments show an average deficiency in bromate amounting to 0.0009 grm., or to 0.64 per cent.

(To be continued).

Suboxide of Bismuth.—S. Tanatar.—The oxalate of bismuthyl, C₂O₄(BiO)₂, is prepared first by digesting Bi₂O₃ with a warm solution containing a known calculated quantity of oxalic acid. The dried salt is calcined as gently as possible in a current of carbonic acid. There remains a black powder of the formula BiO, stable in air, slowly attacked by water, reducing Fehling's solution, and permanganate when warmed. Density at 19° C. = 7.153—7.201. If heated too strongly, a grey powder is obtained, being a mixture of bismuth and Bi₂O₃. As for the oxalate of bismuth and bismuthyl, (C₂O₄)Bi₂O, it gives a mixture of the suboxide BiO and the metal.—*Zeit. Anorg. Ch.*, vol. xxvii., p. 437.

A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM, AND DIDYMIUM, AND ITS APPLICATION TO THE ANALYSIS OF MONAZITE.*

By FLOYD J. METZGER.

THE marked disagreement, among well-recognised chemists, in the determination of thorium in monazite sand, seemed sufficient to warrant a more careful investigation of the methods now existing for its determination, and it was with this object in view that the following work was undertaken.

By thorium, is meant the element as it was generally understood before the more recent researches of Brauner and Baskerville, which point quite conclusively toward the isolation of a new element from what is now generally called thorium.

Review of Methods.

Among the methods proposed for the separation and purification of thorium, the following may be mentioned as the most important.

Bahr (*Liebigs Ann. Chem.*, 1864, cxxxii., 231) was the first to notice that thorium oxalate was soluble in a hot concentrated solution of ammonium oxalate. Since that time numerous investigators, namely, R. Bunsen (*Pogg. Ann.*, 1875, clv., 380), C. Glaser (*Zeit. Anal. Chem.*, 1897, xxxvi., 213), Hintz and Weber (*Zeit. Anal. Chem.*, 1897, xxxvi., 27), and others, have attempted to perfect the separation, and have found that a complete separation of thorium from the other rare earths, in the form of oxalates, cannot be made by one extraction with a hot concentrated solution of ammonium oxalate, but that the operation has to be repeated several times.

The separation of thorium from the other rare earths by using sodium thiosulphate was first proposed by Chydenius (*Pogg. Ann.*, cxix., 46), and later worked by Hermann (*Journ. Prakt. Chem.*, xciii., 106), Drossbach (*Zeit. Angew. Chem.*, 1901, p. 655), Hintz and Weber (*Zeit. Anal. Chem.*, 1897, xxxvi., 676; xxxv., 525), and others.

The separation is based on the fact that thorium is precipitated from a neutral or slightly acid solution by sodium thiosulphate, while cerium and the other rare earths remain in solution.

As was pointed out by Chydenius (*loc. cit.*), and also by Glaser (*Chem. Zeit.*, 1896, xx., 612), the precipitation is not complete in one operation, but by re-precipitating the filtrate with ammonia, converting this into the chloride, and re-precipitating with sodium thiosulphate (repeating as long as a precipitate is obtained with sodium thiosulphate), a complete separation is obtained.

Hintz and Weber (*loc. cit.*) say the separation works best in dilute solutions and in the presence of two or three drops of dilute hydrochloric acid, and give this method preference.

Cleve (*Bull. Soc. Chim.*, 1885, xliii., 53) was the first to show that thorium could be precipitated by hydrogen peroxide from a sulphate solution, and that the precipitate had the composition represented by the formula $\text{Th}_2\text{O}_7\text{SO}_3$.

Boisbaudran (*Comptes Rendus*, c., 605) also used hydrogen peroxide as a precipitant about the same time.

Wyruboff and Verneuil (*Comptes Rendus*, 1898, cxvii., 340), carried the investigation a little farther, and showed that an analogous precipitate of thorium could be obtained from a solution of the nitrate (*i.e.*, $\text{Th}_4\text{O}_7\text{N}_2\text{O}_5$), and that it gave a complete separation of thorium from the other rare earths.

Kosmann (*Chem. Centrbl.*, 1897, Part 1, 837) separated the greater part of the didymium salt from the crude material, as sulphate. Then he separated thorium from

cerium, lanthanum, and didymium by successive treatment of the acid solution with hydrogen peroxide solution, an acid-ammonium citrate solution, and ammonia. A precipitate of aluminum phosphate and thorium hydroxide was formed, which was afterwards separated by oxalic acid.

Various other methods which are well worth mentioning are:—Urban (*Bull. Soc. Chim.*, 1896, xv., 347) used acetylacetone of sodium. Chavastelon (*Chem. Centrbl.*, 1900, i., 876) separated thorium by means of sodium sulphite. Boisbaudran (*CHEMICAL NEWS*, 1884, l., 201; also *Comptes Rendus*, 1884, xcix., 525) precipitated thorium, after reducing the cerium, with cuprous oxide. Dennis (*Amer. Chem. Journ.*, 1894, xvi., 79; also *Journ. Amer. Chem. Soc.*, 1896, xviii., 947) used potassium nitride. Delafontaine (*CHEMICAL NEWS*, 1897, lxxv., 230) separated thorium from zirconium by fusion with potassium acid fluoride, and leaching out the double potassium-zirconium fluoride with hot water. Muthmann and Baur (*Ber. de Chem. Ges.*, 1900, cccxxii., 2028) employed potassium chromate. Kersten (*Pogg. Ann.*, 1839, xlvii., 385) based a method upon the difference in solubility of the oxides in hydrochloric acid. Nilson (*Ber. d. Chem. Ges.*, 1882, p. 2521; 1887, p. 1666) precipitated the hydrated sulphate of thorium.

Undoubtedly the best method which has yet been published for the complete analysis of monazite is that of Glaser (*Journ. Amer. Chem. Soc.*, 1896, xviii., 789).

Benz (*Zeit. Angew. Chem.*, 1902, p. 297) in a recent article, makes a very careful study of the methods now employed for the analysis of monazite (the ammonium oxalate, thiosulphate, and hydrogen peroxide methods), and gives a good comparison of their accuracy.

He finds that one digestion of the mixed oxalates with even a large excess of ammonium oxalate is insufficient to bring into solution all the thorium; on the contrary, he finds that only about one-half the thorium is dissolved, and that after repeated digestions considerable cerium is brought into solution.

With the thiosulphate method he gets very good results after three or four precipitations, and obtains the thorium almost without a trace of cerium. This, however, has the disadvantage of being extremely long.

Hydrogen peroxide, as he shows, precipitates thorium completely from a neutral solution, or from a solution very faintly acid with nitric acid. It also separates thorium from cerium and lanthanum by one re-precipitation.

EXPERIMENTAL.

Various Precipitants Tried.

As very few weak organic acids have hitherto been employed for the separation of thorium from its associated rare earths, the following were tried:—

Maleic Acid.—Aqueous solutions of maleic acid with thorium, cerium, lanthanum, and didymium give no precipitate hot or cold. Solutions of cerium, lanthanum, and didymium, in 50 per cent alcohol, give nothing hot or cold. A solution of thorium in 50 per cent alcohol gives no precipitate in the cold, but on heating, a partial precipitation results.

Cinnamic Acid produces at least a partial precipitation of thorium from 20 per cent alcoholic solutions. The precipitate cannot be filtered (runs through), and for this reason the completeness of the precipitation was not determined. Cerium, lanthanum, and didymium give nothing under the same conditions.

Picric Acid and thorium, in alcoholic solutions, give a partial precipitation of thorium. Cerium, lanthanum, and didymium give no precipitate under these conditions.

Phthalic Acid in aqueous solution with cerium, lanthanum, and didymium gives nothing cold or hot. Thorium, however, in aqueous solution with phthalic acid gives a partial precipitation on heating. From alcoholic solutions a heavy curdy precipitate results on heating, and is approximately half complete. Cerium, lanthanum,

* Contribution from the Havemeyer Laboratories, Columbia University. Read at the meeting of the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxiv., No. 10.

and didymium in alcoholic solutions with phthalic acid give no precipitate.

Fumaric Acid.—Aqueous solutions, hot or cold, give nothing with cerium, lanthanum, or didymium. Thorium and fumaric acid in aqueous solutions give a precipitate in the cold, which forms slowly, but on applying heat the precipitate forms rapidly (white, flocculent), settles out nicely, and is almost complete. From solution in 95 per cent alcohol, fumaric acid precipitates thorium quantitatively even in the cold. Cerium and fumaric acid in 95 per cent alcohol give no precipitate in the cold, but, on heating, a small fraction of the cerium is thrown down. Lanthanum and didymium in 95 per cent alcohol give nothing cold or hot. From solutions in 40 per cent alcohol, fumaric acid gives a quantitative precipitation of thorium on heating; lanthanum and didymium under the same conditions give nothing. Cerium in 40 per cent alcohol gives, with fumaric acid, nothing cold or hot, unless the cerium solution is quite strong, when a very small fraction is precipitated.

Ammonium Fumarate precipitates thorium, cerium, lanthanum, and didymium from aqueous solutions, insoluble in excess, soluble in mineral acids.

Among the amido and amino compounds tried were:—
Urea gave nothing.

Thiourea gave nothing.

Acetamide gave nothing.

Semicarbazine gave nothing.

Succinimide gives no precipitation of cerium, but gives a partial precipitation of thorium from alcoholic solutions.

Diethylamine precipitates thorium, cerium, lanthanum, and didymium.

The Quantitative Precipitation of Thorium by Fumaric Acid.

From the experiments given on a preceding page it was now evident that thorium could be precipitated quantitatively from alcoholic solutions, leaving cerium, lanthanum, and didymium in solution. It was desirable to know the smallest quantity of alcohol necessary to effect this precipitation, and still leave the cerium, lanthanum, and didymium in solution. This strength was reached when the solution contained 40 per cent of alcohol.

The following results will show the completeness of the precipitation from the various strengths of solution:—

Alcohol. Per cent.	Volume. C.c.	ThO ₂ .	
		Taken.	Found.
15	150	0.1568	0.1508
35	150	0.1568	0.1551
40	200	0.1961	0.1962
40	150	0.1568	0.1561
40	120	0.1176	0.1176
40	120	0.2007	0.2003
40	100	0.1004	0.1006
40	120	0.1176	0.1179
40	200	0.1961	0.1962

Separation of Thorium from Cerium, Lanthanum, and Didymium.

The salts used for the experiments were the best nitrates that could be purchased, and the thorium nitrate was purified according to the method suggested by Wyruboff and Verneuil (*Comptes Rendus*, 1898, cxxvi., 4, 340), which is as follows:—

Eighty-three grms. of the nitrate, corresponding approximately to 39 grms. of thorium, were dissolved in 8 litres of water. The solution was divided equally in twelve beakers, and precipitated with hydrogen peroxide (10 c.c. hydrogen dioxide for every 0.5 gm. thorium dioxide). The solutions were then heated to 85° C., and allowed to settle. The precipitates were washed a dozen times by decantation with hot water, and then transferred to a large Büchner funnel, and the washing continued until the filtrate gave no precipitate with ammonia. The precipitate was then transferred to a large porcelain

evaporating dish, and 150 c.c. of concentrated nitric acid added; heat was applied, and the whole went into solution readily. The solution was evaporated to dryness, taken up in water, diluted to 8 litres, and the process repeated. The filtrate from the hydrogen peroxide precipitation was treated with ammonia and hydrogen peroxide, giving a brown precipitate of cerium trioxide. This precipitate of cerium peroxide was examined for lanthanum and didymium, but none could be detected.

A stock solution was made of this purified thorium nitrate and standardised very carefully by precipitation with oxalic acid. This was the thorium used for the experiments. A cold saturated solution of fumaric acid in 40 per cent alcohol (containing approximately 0.1 gm. per 10 c.c.) was used as the precipitant.

(To be continued).

NOTICES OF BOOKS.

The New Volumes of the Encyclopædia Britannica. The Sixth of the New Volumes, being Vol. XXX. of the Complete Work. London: *The Times*. Edinburgh: Adam and Charles Black. 1902. Pp. 845.

THIS volume of the *Encyclopædia Britannica* comprises those subjects whose titles fall between the alphabetical headings K A B (Kabadian) and M O R (Morvi).

The first article of chemical interest in this volume is one on "Lead," by Mr. H. O. Hofman, Ph.D., in which he draws attention to the important changes in lead-smelting introduced during the last twenty years of the nineteenth century, particularly in America. By the modern method about half the lead is extracted at a very low temperature, leaving rich slags, containing 50 per cent of lead, to be smelted in the blast-furnace, the ultimate result being a very much higher yield than by the other older processes. The reverberatory furnace method, cupelling, the Pattinson and the Parkes process, for smelting and refining lead, are also described.

A long article on "Light," by Mr. C. G. Knott, D.Sc., next claims attention. After a few remarks on the wave theory, we come to photometry and light standards, and here a number of photometers are described. The refraction and dispersion of light are dealt with next, after which we come to polarised light, and the relative motions of matter and æther.

The most important article in this volume, speaking scientifically, is the one contributed by Professor James Dewar, F.R.S., on "Liquid Gases." The article is mainly confined to the discussion of the properties of liquid atmospheric air and the so-called permanent gases—oxygen, nitrogen, and hydrogen—and is a subject Professor Dewar has made peculiarly his own. The article covers twelve pages, and is well illustrated. With regard to the industrial applications of liquid air Professor Dewar does not speak very hopefully. Its use as a source of motive power is, he says, impracticable for any ordinary purpose on the score of inconvenience and expense. Still, in conditions where economy is of no account, liquid air might perhaps, with effectively isolated storage, be utilised as a motive power, e.g., to drive the engines of submarine boats, and at the same time provide a supply of oxygen for the crew.

"Magnetism" is ably treated by Mr. Shelford Bidwell, F.R.S., in an article which contains a short account of the general experimental work in magnetism which has been carried out since the publication of the ninth edition of the *Encyclopædia Britannica*. Special branches of the subject are "Terrestrial Magnetism," by Mr. Charles Chree, F.R.S.; "Magneto-Optics," by Professor J. J. Thomson, F.R.S.; and "Measuring Instruments," by Professor J. A. Fleming, F.R.S.

In the table of the principal contents of this volume we

observe that there should be an article on "Metallurgy," by Sir W. C. Roberts-Austen, F.R.S.; we are disappointed to find that no such article is given; the more so as metallurgy is a very important English industry. There is a short one, however, entitled "Metallography," by the above-named author, in which he refers to the importance of the microscopical examination of metals and alloys has assumed in recent years. A full-page plate is given, containing reproductions of six excellent microphotographs of a gold-copper alloy, three different steels, a gold-lead alloy, and a lead-antimony alloy. The apparatus for taking these photographs is described and illustrated.

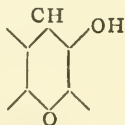
Among the articles of more general interest contained in this volume, we may mention "Military Kites," by Major B. F. S. Baden-Powell; "De Lesseps," by M. de Blowitz; "Lighthouses," by W. T. Douglass; "Machine Guns," by Major H. W. Barlow, R.A.; and "Magic," by J. N. Maskelyne and G. Faur.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

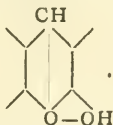
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 14, October 6, 1902.

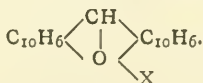
A Derivative of Hydrogen Peroxide.—R. Fosse.—In a former paper the author showed that dinaphthapyranol, $C_{10}H_6 < \begin{smallmatrix} \text{CHOH} \\ \text{O} \end{smallmatrix} > C_{10}H_6$, in acetic solution possesses a certain oxidising power. The action of dinaphthopyranol on reagents, such as powdered zinc, alcohol, pyrogallol, and the alkaline iodides, shows clearly that this body in acetic solution cannot be considered as an alcohol of pyranol,—



but as a hydrogen peroxide derivative of the hydrate,—



It is known that the first of these peroxides prepared, that of ethyl, was obtained by M. Berthelot, and MM. Baeyer and Villiger have since prepared a great number of peroxides and hydrates of these peroxides. The formula of the author's new peroxide hydrate can be obtained by replacing X by OH in the general formula,—



Synthesis of certain Tertiary Alcohols. Diphenylcarbinols.—H. Masson.—The author examines the action of magnesium phenylbromide on various ethers; ethyl formate alone giving a secondary alcohol—benzhydrol, $(C_6H_5)_2CH.OH$, melting at 63° . The ethers of the other acids give tertiary alcohols of the form $(C_6H_5)_2COH$ —R. These are usually crystalline, and cannot be distilled *in vacuo* without loss of water. Distillation at ordinary pressure leads to the formation of the corresponding ethylenic carbides. The carbides thus produced are not often crystalline; they fix two atoms of

bromine, giving liquid dibromine derivatives. On oxidation they give benzophenone and acids having one carbon atom less than the generating acid. On hydrogenation by alcohol and sodium the corresponding saturated carbides are formed.

Anhydrous Cupro-ammonium Sulphates.—M. Bouzat.—The author examines the cupro-ammonium sulphates in order to compare their heats of formation with those of the chlorides. It is already a known fact that the different cupric salts dissolve, evolving the same quantity of heat, when combining with ammonia, and that this relation shows the existence of complex radicals transporting themselves without alteration from one ammonium salt to another. The author now applies the same theory to solids. For this purpose, he prepares various cupro-ammonium sulphates and measures their heats of formation.

Researches and Estimation on the Extract of Chestnut Tree mixed with Extract from Oak Tree.—Ferdinand Jean.—When a solution of the extract of chestnut wood is agitated with a solution of iodic acid in the cold a certain quantity of iodine is liberated, whilst with an extract of oak wood this phenomenon does not take place. The reaction is equally negative with solutions of mangrove, mimosa, sumac, mastic tree, fustic, and thorn; logwood is an exception, and liberates a small quantity of iodine. The extracts of oak wood prepared for tanning being frequently falsified with an extract of chestnut wood, it is interesting to find a means of detecting this fraud, which hitherto has not been punishable, owing to the fact of there being no chemical means of recognising it.

Pectic Fermentation.—M. Goyand.—When certain vegetable juices are added to a concentrated aqueous and neutral solution of pectine, the mixture becomes a gelatinous mass. This phenomenon is produced by the diastase pectase. It is known that pectase only acts in presence of calcium salts and in a slightly acid solution. The author's present research is to prove that, in the absence of calcium salts, pectase has an action on pectine, and he finds that it transforms pectine into pectic acid, even in the absence of calcium salts. The phenomenon is visible, on account of the formation of insoluble calcium pectate. If, however, the lime is replaced by potash, in the form of potassium oxalate, a potassium pectate soluble in water is produced. These experiments were undertaken with the purpose of finding under what conditions the lime is precipitated by the oxalate of sodium and ammonium. The results are similar in all cases. Another means of verifying this fact is that a neutral molecule of pectine gives one or more molecules of pectic acid, and the acidity of the mixture increases. To verify this hypothesis, it is necessary to use small proportions of pectase, in order that the transformations may not be too rapid. A table of the results obtained is given, and from them the definite conclusion is drawn that pectase is formed from pectic acid by means of pectine, and that the phenomenon is not influenced qualitatively by the presence or absence of calcium salts.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 7.

A New Gaseous Body: Hexafluoride of Sulphur, SF_6 .—H. Moissan and P. Lebeau.—A preliminary experiment of placing a fragment of sulphur in contact with fluorine gas showed that at least two new compounds were formed:—(1) A gaseous body, on which water is without action and which is absorbed by a solution of potash; (2) a gaseous body non-absorbable by water and alkaline solutions, and decomposed by sodium vapour. By using an excess of fluorine the unabsorbable gas is the one formed in the greatest quantity; it may even reach 80 or 90 per cent. It is easily obtained in a state of purity by treating the mixture of the two fluorides with a solution

of potash. As this new body was produced in an excess of fluorine, it was reasonable to suppose that it would be a perfluorised compound of sulphur; this was proved to be the case. Hexafluoride of sulphur, SF_6 , is a colourless, odourless, tasteless, incomcombustible gas, and does not support combustion. It solidifies at about -55° , forming a white crystalline mass. The gas is very slightly soluble in water, and slightly soluble in boiled anhydrous alcohol. Although so rich in fluorine, it is curious to observe that it is, as a rule, inert, and its properties are comparable with those of nitrogen. Oxygen only reacts on this gas at the temperature of a strong induction spark, sulphur is without action at its fusing-point, though its vapour attacks the gas. Vapour of selenium decomposes fluoride of sulphur, but the reaction is not very definite. At the temperature of softening glass sulphuretted hydrogen reacts easily, depositing sulphur and producing white fumes, which condense, forming colourless drops. Ammonia-gas, either cold or at a red heat, has no action on fluoride of sulphur.

Density and Analysis of Hexafluoride of Sulphur.—H. Moissan and P. Lebeau.—The density of this perfluoride of sulphur was determined by means of the apparatus devised by MM. Moissan and Gautier (*Ann. Chim. Phys.*, Series 7, vol. v., p. 56), and the following figures were obtained:—4'95, 4'99, 5'09, 5'11; the theoretical figure for SF_6 being 5'06. The fluorine was estimated gravimetrically by decomposing the gas with metallic sodium vapour and estimating the fluorine in the fluoride of sodium formed. The figures obtained were—78'40, 78'62, 79'10; the theoretical figure for SF_6 being 78'08. The estimation of the sulphur gave 22'00 and 22'25, against the theoretical figure 21'91 for SF_6 .

Preparation, Properties, and Analysis of Fluoride of Thionyl.—H. Moissan and P. Lebeau.—Fluoride of thionyl is prepared by passing fluorine gas over chloride of thionyl, the temperature being kept down to about 0° . The flask in which the reaction takes place is connected with another one kept at -80° , in which the fluoride of thionyl is liquefied. The gas thus obtained is not pure, but contains a little chlorine, which can be removed by agitation with mercury; it also contains oxyfluoride of sulphur, which can be eliminated by a series of liquefactions and fractional distillations. Fluoride of thionyl is a colourless gas, fuming slightly in moist air, with a suffocating odour as disagreeable as that of oxychloride of carbon. Its boiling-point is about -32° . Its density in three determinations gave 3'04, 2'90, 2'88; theory gives 2'97. It is soluble in chloride of arsenic, essence of turpentine, and benzene. The action of heat on fluoride of thionyl in the presence of glass enables us to determine the composition of this gas volumetrically. Four volumes of SOF_2 ought to give four volumes of SO_2 and two volumes of SiF_4 .

	Volume of gas.	SiF_4 .	SO_2 .
Found	6'8	3'1	6'1
Calculated ..	6'8	3'3	6'3

A known volume of fluoride of thionyl is treated with water. When the absorption is complete, the liquid is treated with a titrated solution of iodine, and the sulphur estimated. In the liquid, the fluorine is precipitated as fluoride of calcium; at the same time a little sulphate of calcium is deposited. The mixture is dried and weighed, then converted entirely into sulphate, by which means the fluorine can be determined. The following figures were obtained:—

		Theory.
Fluorine	44'10	44'40
Sulphur	36'30	36'85
		37'1

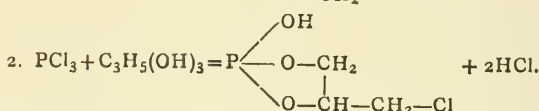
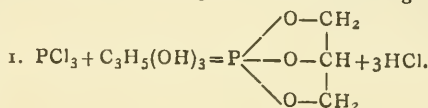
A New Oxyfluoride of Sulphur: Fluoride of Sulphuryl, SO_2F_2 .—H. Moissan and P. Lebeau.—Already noticed.

Electrolytic Preparation of Antimonide of Lithium, and Some Alloys of this Metal.—P. Lebeau.—Already noticed.

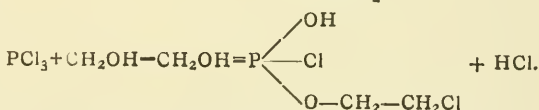
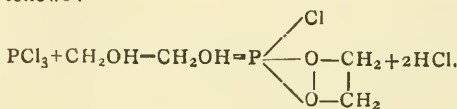
A new Preparation, and the Properties of Antimonide of Lithium.—P. Lebeau.—Already noticed.

Etherification of Phosphorous Acid by Glycerin and Glycol.—P. Carré.—Already noticed.

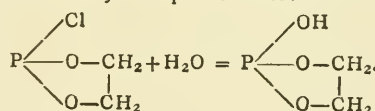
Action of Trichloride of Phosphorus on Glycerin and Glycol.—P. Carré.—The author is of the opinion that the reaction of trichloride of phosphorus on glycerin takes place according to the two following equations:—



An analogous research has led him to the conclusion that the action of trichloride of phosphorus on glycol is as follows:—



Only the first of these ethers has been examined; its action on water may be expressed thus:—



Some Derivatives of *p*-Sulphochloride of Toluene and of *o*-Nitro-*p*-sulphochloride of Toluene.—F. Reverdin and P. Crépieux.—Already noticed.

Action of Oxidising Agents on Pentachlorophenol.—E. Barral.—By oxidation with fuming nitric acid, hexachlorophenol- α is transformed integrally into tetrachlorised quinone or chemically pure chloranil; but the author found that, not only did none of the principal oxidising agents transform pentachlorophenol into quinone, but many of them did not give chloranil, while others destroyed the pentachlorophenol to a great extent, forming a minimal fraction of chloranil.

Transformation of Pentachlorophenol into Tetrachlorised Quinone.—E. Barral.—By reacting with oxidising agents on pentachlorophenol the author observed the following facts:—1. Whenever chloranil is formed, most of the pentachlorophenol is destroyed. 2. When chloranil is formed, its formation is preceded by that of hexachlorophenol- α , on which the oxidising agent reacts, transforming the ketone into diketone. 3. On passing chlorine through hydrochloric acid holding pentachlorophenol in suspension in the cold, he obtained another intermediate body—heptachlorophenol- α , $\text{C}_6\text{Cl}_7\text{OH}$,—fusible at 98° , decomposing at 130° into hydrochloric acid and hexachlorophenol, $\text{C}_6\text{Cl}_6\text{OH} = \text{C}_6\text{Cl}_6\text{O} + \text{HCl}$.

Examination of the Essence of Sweet Orange Blossoms.—E. Theulier.—Already noticed.

Catalytic Properties of the Hydrogenases. Identification of M. Loew's "Catalase" and of M. de Rey-Pailhade's "Philothion."—The result of a very long paper is to show that these two diastases are identical; they have a characteristic reaction, viz., they reduce ferricyanide of potassium to which ferric chloride has been added.

MISCELLANEOUS.

F. E. Becker and Co. (W. and J. George, Ltd., Successors).—We have just received the new Illustrated Catalogue and Price List of Balances, Scales, and Weights issued by this well-known firm. Messrs. George, Ltd., are not only importers of these goods, but are also manufacturers, and undertake repairs and adjustment of the same. This catalogue is very well got up, and it is claimed by the firm to be the largest and best illustrated catalogue in the world devoted entirely to balances and weights. The firm is one of world-wide reputation, and we hope their success will continue. We would call attention to the special balance, illustrated on page 60, manufactured according to Mr. Kuhlmann's design; this balance is constructed with mechanism for rapidly placing and removing the weights; it will carry 200 grms. in each pan, and is sensitive to $\frac{1}{1000}$ th of a mgrm. when fully loaded. On the right-hand side of the case protrude a number of transporters, one for each weight, each being plainly marked with the weight it carries; by this means any number of weights can be placed on, or removed from, the pan very rapidly, while the case remains closed the whole time. By means of an automatic arrangement, on placing a weight on the pan the figure corresponding to its value appears at the side, and disappears when the weight is removed, so that the final reading can be made accurately and almost at a glance.

Synthetic Formation of Ammonia.—E. Baur.—The electrolysis of an aqueous solution of nitrate of ammonium saturated with ammonia gas (Divers's solution) gives, at the two poles, hydrogen and nitrogen respectively in the proportion of 3 to 1. Inversely, if we set up a Grove's cell with these two gases over the Divers solution, we observe a tendency towards their re-composition, shown by an electromotive force of 0.6 volt. The phenomena are very similar if we replace the NO_3NH_4 by KCl. The author has also examined the variation of the electromotive force with the temperature. No trace of ammonia was found by heating the mixture $\text{N}+3\text{H}$ with platinum black, or with nitrides of chromium or molybdenum, or by leaving the same mixture, in the cold, in contact with platinum foil and a little hydrochloric acid.—*Berichte*, vol. xxxiv., p. 2385.

Quadrantoxide of Cadmium.—S. Tanatar.—Oxalate of cadmium is calcined at as low a temperature as possible in a current of dry carbonic acid, taking care to stir from time to time; the operation is stopped when no more gas comes off, and the material allowed to cool in the carbonic acid. A beautiful green powder remains, stable in dry air, oxidised slowly by cold water, and decomposed by acids or by ammonia into metallic cadmium and CdO . Its formula is Cd_4O , and its density at 19° is 8.177–8.207. If heated too strongly during its preparation, a yellowish brown powder is obtained, which is a mixture of the metal and the protoxide.—*Zeit. Anorg. Ch.*, vol. xxvii., p. 432.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Sodium Bismuthate.—I should like to know how "sodium bismuthate" (mentioned in *CHEM. NEWS*, lxxxiv., p. 209), for oxidation of manganese, is prepared, as I cannot find it in any of the ordinary text-books.—S. C.

Potassium Persulphate.—An attempt was made to prepare potassium persulphate by electrolysis of a saturated solution of KHSO_4 (Kahlbaum's pure) with a thermopile, which gave a current of 4 amperes; the experiment was allowed to continue for 124 hours (overnight) but at the end of that time absolutely no persulphate was formed. The KHSO_4 solution was placed in a platinum dish, which was surrounded by cold water; in the platinum dish was placed a small porous pot containing dilute H_2SO_4 ; the dish was connected

with the anode by a piece of clean platinum, and dipping in the sulphuric acid was a similar piece of foil connected with the cathode; there was a good contact between the dish and foil. Would be very much obliged if some kind reader would give probable cause of failure, or a simpler and better method (if any) of preparing small quantities (20 to 40 grms) of potassium persulphate, or even ammonium persulphate—the potassium salt preferred.—S. C.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 3rd.—Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "Preliminary

Investigation of the Chemical Changes produced by various Reagents on Gutta-percha," by Sir William Ramsay. "The Reduction of Ammoniacal Silver Solutions by Organic Substances," by Dr. G. T. Morgan. "A Simple Qualitative Test for Bromides and Iodides," by Dr. F. Mollwo Perkin. "The Influence of Impurities on the Specific Gravity of Sulphuric Acid," by Arthur Marshall.

WEDNESDAY, 5th.—Society of Public Analysts, 8. "Reactions of the Alkaloids of *Ipecacuanha*" and "The Analysis of Preparations containing Opium," by Alfred H. Allen, F.I.C. "Estimation of Salicylic Acid," by Sidney Harvey, F.I.C. "Volatility of Aqueous Solutions of Acetic Acid," by Wm. Chattaway, F.I.C.

THURSDAY, 6th.—Chemical, 8. "Di-indigotine," by J. Moir. "Localisation of Phosphates in the Sugar-cane," by C. H. G. Sprankling. "Specific Heats of Gases," by H. Crompton. "Non-existence of the Gaseous Sulphide of Carbon described by Deninger," by E. J. Russell and N. Smith. "Action of Nitric Acid on Bromophenolic Compounds," by W. Robertson. "Hydroxyoxamides, Part II.," by R. H. Pickard, C. Allen, W. A. Bowdler, and W. Carter. "3:5 Dichloro-o-xylene and 3:5 Dichloro-o-phthalic Acid," by A. W. Crossley and H. R. Le Sueur. "Isometric Anhydrous Sulphates of the Form $\text{M}^+\text{SO}_4\text{R}^+\text{SO}_4$," by F. R. Mallet. "Catalytic Racemisation of Amygdaline," by J. W. Walker. "Combination of Carbon Monoxide with Chlorine under the Influence of Light," by G. Dyson and A. Harden. "Constituents of Commercial Chrysarobin," by H. A. D. Jowett and C. E. Potter.

APPOINTMENT OF EDITOR.

The Council of the CHEMICAL SOCIETY invite applications for the office of EDITOR. The duties will be to Edit the "Journal" and "Proceedings" of the Society and to supervise the preparation, by the Sub-Editor and Abstractors, of the Abstracts of foreign Papers published in the "Journal."

The appointments will be made from 1st January, 1903. Applications, accompanied by full particulars, must be received before WEDNESDAY, NOVEMBER 12, 1902, addressed to the Hon. Secretaries, Chemical Society, Burlington House, Piccadilly, London, W., from whom further particulars may be obtained.

PATENTS, DESIGNS, AND TRADE MARKS ACTS
1883 TO 1888.

NOTICE IS HEREBY GIVEN that

REGINALD EATON ELLIS of 70 and 72 Chancery Lane in the County of London seeks leave to Amend the complete Specification of his invention left in connection with his application for Letters Patent, No. 14049 of 1902, for "Improvements in or relating to the manufacture of Indoxyl or Indigo, or Indoxyl or Indigo preparations."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents), issued on the 22nd October, 1902.

Any person, or persons, may give Notice of Opposition to the Amendment (on Form G), at the Patent Office, 25, Southampton Buildings, London, W.C., within one calendar month from the date of the said Journal.

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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2241.

LABORATORY NOTES.

By HORACE JERVIS.

Carbon by Combustion.—The estimation of carbon in metals by combustion is perhaps the most elaborate assay the iron-works analyst ventures upon. It is much more elaborate as a matter of tradition than it need be as a matter of fact, and this to some extent accounts for its entire absence from some works, and its meagre practice in some colleges professedly fitted with the most modern apparatus for the rapid and accurate analysis of iron and steel.

The only alternative to carbon by combustion is the Eggertz colour test, whose advantageous use is strictly limited to comparative cases, and whose indications are considerably vitiated or entirely upset by varying amounts of elements—other than carbon—which occur commonly in steels. It is a matter of some moment, therefore, to reduce the combustion process to its simplest forms.

Changing Boats.—Boats containing the carbonaceous residue are sometimes changed while the tube is at full redness, so as to economise the time needed for the actual combustion. There is a slight back pressure immediately the stopper is replaced, but it occasions no loss if everything is done smartly. If desired, the aspirator can be attached and allowed to act during the changing, as the small amount of unpurified air thus drawn into the tube has no significant effect on the result; e.g., two and a-half litres of such air increased the weight of a potash bulb 3½ m.grms. only. The boats should be dry and warm when taken from the bath, so as to lessen the danger of cracking the tube. To lower the temperature of the entire furnace with the same object is a bad practice, as it allows CO to pass the barely red CuO without being oxidised.

Copper Oxide.—Copper oxide, kept at a red heat, is essential whenever the carbonaceous residue is burned slowly at increasing temperatures; but if the boat is pushed at once into a tube heated to bright redness, no appreciable amount of carbon monoxide is formed, and the copper oxide may be omitted. It is not desired to suggest that the author prefers to work with an entirely empty combustion tube, but merely to state that the results of a series of estimations made in that way varied in no case more than 0.02 per cent from those obtained in the usual manner. Where, however, the direct combustion of a steel, after mixing with red-lead, is practised, the use of an empty tube is recommended. It may be remarked, in parenthesis, that the direct combustion of steel borings with some oxidising reagent is essential for the accurate assay of samples containing large amounts of chromium and tungsten, such as are now made for taking deep cuts at high speeds; the results are low whenever a preliminary separation of the iron and carbon is made.

Furnace Blanks.—When air or oxygen is passed through a combustion furnace, the attached potash-bulb or soda-lime tube nearly always weighs more (or less) after the operation than it did before. This difference is not due, as is often supposed, to an imperfection in the furnace-tube or an impurity in the asbestos which accompanies the separated carbon. It is due almost entirely to an unequal desiccation of the gases as they enter and leave the potash-bulb. The question, therefore, of whether the calcium chloride prolong can completely dehydrate the gases is not very important; its efficiency depends on its accurate adjustment to the desiccating arrangements which stand before it in the train of purifiers. This adjustment is best attained by drying the material as bought in a uniform

manner. Even then perfection is not attained, and a blank determination is essential, and must be repeated as the calcium chloride becomes visually moist along the length of the prolong.

Gravimetric Estimation of Sulphur.—The most troublesome part of this process is the evaporation of the nitro-hydrochloric acid solution of the steel to dryness. The tendency to spirt is very small until the clear dark solution shows signs of turbidity; up to this point, therefore, half a plate-full of samples may be safely boiled at a brisk rate. It is then most expedient to pass a rubber or leather strap round the uncovered beaker, and whirl it over a strong Bunsen flame. A hissing noise is heard until the mass becomes so thick that it can hardly move, and then a decided crackling may be noticed. When this is over, i.e., in about two minutes, the beaker may be placed on the hottest part of the plate without fear of spirting; but as the basic nitrates have dried partly up the sides of the beaker, it is better to replace the cover and allow it to stand in a less heated position so that the acid fumes may condense and run down the sides of the beaker. In this way the material is neatly collected on the bottom, and can be most effectively baked.

ON ANTIMONY PENTIODIDE.

By R. W. EMERSON MACIVOR, F.I.C., &c.,
Formerly Assistant Professor of Chemistry, Anderson's College
(Medical Faculty), Glasgow.

IN a paper read before the Chemical Society of London many years ago (*Chem. Soc. Journ.*, 1876, vol. i., p. 329) I contradicted the statement previously made by van der Espt (*Arch. Pharm.*, [2], cxvii., p. 115), that antimony pentiodide is formed when a mixture of the elements in the required proportions is carefully heated, and also showed that it is not produced when antimony tri-iodide and iodine are brought together (with or without heat), either in the solid form or in solution in carbon disulphide; indeed, the results of my investigation led me to conclude that the pentiodide does not exist.

Pendleton, however, states (*CHEMICAL NEWS*, vol. xlviii., p. 97) that he succeeded in forming the compound by fusing antimony with an excess of iodine in an atmosphere of inert gas in a sealed tube kept at a temperature above the fusing-point of the mixture for an hour or two, the excess of iodine being subsequently removed by heating the material at a temperature not exceeding 130° C. The final product was found to have a composition corresponding "pretty closely" with SbI₅, and "consisted of a homogeneous mass of crystalline structure and dark brown colour, distinctly different from the tri-iodide, decomposable by water or on prolonged exposure to moist air." The melting-point of the substance is given as being between 78–79°, notably lower than that of either the tri-iodide or iodine.

I made a quantity of the supposed SbI₅ in the manner described by Pendleton, conducting the operation in an atmosphere of pure dry carbon dioxide, and submitted it to careful examination, with the result that, however its low melting-point may be explained, I have formed the opinion that it consists of an intimate mixture of the tri-iodide and iodine.

On analysis (the iodine being determined by means of sodium thiosulphate) it was found to contain 80.153 per cent of iodine (126.9), theory for SbI₅ requiring 84.151; but after continuous heating for twelve hours at 125–130° in a slow current of dry carbon dioxide, this fell to 76.373 per cent; theory for SbI₃ being 76.032. It dissolved in hot carbon disulphide, yielding a solution possessing the characteristic colour imparted to that liquid by free iodine, and which, on cooling, deposited crystals of SbI₃ melting at 165°. By means of chloroform, in which the tri-iodide is only slightly soluble, I succeeded in completely dissolving out the free iodine from the substance,

and obtained pure SbI_3 . On being decomposed by water the material yielded yellow oxyiodide, hydriodic acid, and much free iodine—a result to be expected from such a mixture as I believe Pendleton's product to be.

The Laboratory, 29, Fenchurch Street, E.C.

NEW METHOD FOR PURIFYING POTABLE WATERS.

By P. GUICHARD.

A FEW years ago (*Bull. Soc. Chim.*, Series 3, vol. xix., p. 588) I read, before the Société Chimique, a paper on the action of metals and of organic matter on the permanganates. From the experiments described in this paper, I devised a method for the purification of potable waters, which consists of acting on the waters with permanganate of lime in excess for a sufficient time, and then destroying the excess of permanganate with iron; it is then only necessary to filter to separate the insoluble ferric and manganic oxides.

This filtration was the difficult part of the operation; at first I used a filter of absorbent cotton-wool, but the difficulty of arranging this in a convenient and practical manner caused me to abandon it, and to use instead a filter-press containing one or two sheets of sterilised paper. The filtration is very simple then, only it is necessary to change the paper more often than the cotton-wool; however, this changing is very easy and gives no trouble. While the cotton-wool lasted for several months, the paper must be changed once a week. Under these conditions we obtain a perfectly clear liquid, but if we continue filtering, we observe, after about twelve days, according to the amount of water consumed, that the filtered water, which is colourless at first, becomes yellow after a few minutes, and then gradually becomes more and more cloudy, and deposits ferric oxide.

Why does the water, which has kept clear for several days, suddenly become cloudy? For an explanation, it is necessary to examine into the phenomena closely. On leaving the vessel containing the iron, all the iron oxide is in the ferrous state, and is in great excess; this oxide combines with the carbonic acid in the water, forming ferrous carbonate, which is then dissolved in the excess of carbonic acid, but the ferrous oxide saturates this carbonic acid, and nothing remains in the water but neutral ferrous carbonate. Thus we have a very dilute solution of ferrous carbonate, since the carbonate is not at all easily soluble; this solution then passes into the filter. If, in the first place, we decant a portion of the clear solution, we observe that it becomes cloudy after a few moments, and deposits ferric oxide; if, on the other hand, we filter a small quantity, we obtain a clear liquid which does not become cloudy.

I believe that during filtration the cellulose molecule decomposes the ferrous carbonate, fixes the oxide of iron, becomes a mordant, and the water passes free from iron; so long as the cellulose is not saturated with iron, the water passes clear and remains limpid; but when the cellulose becomes saturated with the mordant, the water first passes clear and then becomes cloudy rapidly. Analogous facts in the chemical action of filter-papers have been observed before. Further, through the saturation of the free carbonic acid, the carbonate of lime is precipitated.

In my 1898 paper I endeavoured to reduce the permanganate by means of other metals than iron; nearly all metals reduce the permanganates, but none are so rapid in their action as iron, from which it follows that only iron can effect a reduction sufficiently rapid to give continuous purification. Still, in certain cases, other metals can be employed with advantage if the surface is increased to a sufficient extent to augment the rapidity of the action.

I have used sheets of pure tin-foil with success. The

decolouration of permanganated water by tin takes place about twenty minutes after contact. This is rather a long time, but under certain circumstances, when only a little water is required for example, or when travelling, this is no drawback, as the apparatus is more simple and easy to use.

It suffices to fill a water-bottle with clean sterilised tin-foil, and to pour the permanganated water on it. The water-bottle is then attached to the filter, and the whole reversed over another water-bottle. The filtration is very rapid and easy on account of the absence of iron; nothing remains on the filter except a little manganic oxide. The simplicity of the apparatus and the rapidity of filtration compensate for the slight increase of time necessary for the decolouration of the permanganate.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 18.

THE ESTIMATION OF BROMIC ACID BY THE DIRECT ACTION OF ARSENIOS ACID.*

By F. A. GOOCH and J. C. BLAKE.

(Concluded from p. 217).

PORTIONS of this bromate were taken for reduction by arsenious acid. Solutions not exceeding 200 c.m.³ in volume, containing the bromate and a considerable excess of arsenious oxide acidified with sulphuric acid of half-strength, were boiled for periods varying from ten to forty-five minutes, neutralised with potassium acid carbonate, and titrated with iodine. The results are shown in Table III.

TABLE III.

	KBrO ₃ taken. Gm.	As ₂ O ₃ taken. Gm.	H ₂ SO ₄ (1:1). C.m. ^s . Mins.	Time.	As ₂ O ₃ un- changed. Gm.	As ₂ O ₃ oxidised. Gm.	Error, in terms of KBrO ₃ . Gm.
1.	0.0701	0.1881	5	10	0.0661	0.1220	0.0014 —
2.	0.0701	0.1881	5	10	0.0650	0.1231	0.0009 —
3.	0.0701	0.2475	5	10	0.1232	0.1243	0.0002 —
4.	0.0701	0.2475	5	10	0.1236	0.1239	0.0004 —
5.	0.0701	0.2475	5	25	0.1234	0.1241	0.0003 —
6.	0.0701	0.2475	5	25	0.1234	0.1241	0.0003 —
7.	0.1402	0.4950	3	15	0.2479	0.2471	0.0012 —
8.	0.1402	0.4950	3	15	0.2476	0.2474	0.0010 —
9.	0.1400	0.6188	7	20	0.3708	0.2480	0.0004 —
10.	0.1400	0.6188	7	20	0.3710	0.2478	0.0005 —
11.	0.1400	0.6188	7	20	0.3706	0.2482	0.0003 —
12.	0.1400	0.6188	7	30	0.3708	0.2480	0.0004 —
13.	0.1400	0.6188	7	45	0.3711	0.2477	0.0006 —

Here again, as in the experiments of Table I., the indications of the process of reduction of the bromate by arsenious acid point to a slight deficiency in the oxidising power of the bromate. The mean deficiency, 0.0006 gm., differs from the indications of the process of reduction of the same sample by the potassium-iodide method by about 0.0003+ gm.

The question now arises as to what is the impurity in the bromate. In a product re-crystallised several times, and in one in which no chloride can be detected, as was the case with the bromate of these experiments, the impurity most natural to look for is potassium chlorate, which might resist removal in the process of purification by re-crystallisation. The preparation of bromate upon which these last experiments were made was therefore tested by igniting it and treating the residue with potassium bichromate and sulphuric acid, volatilising and collecting any chloro-chromic anhydride thus formed, and converting the last into lead chromate (Gooch and Brooks, *Am. Journ. Sci.*, 1890, xl., p. 287). Traces of chlorine were thus found, which, not appearing in a similar test upon the unignited bromate, must have had their origin in

* Contribution from the Kent Chemical Laboratory of Yale University. From the *American Journal of Science*, [4], xiv., No. 82.

chlorate intercrystallised with the bromate. In a former paper from this laboratory (Gooch and Smith, *Am. Journ. Sci.*, 1891, xlii., p. 220) it has been shown that a chlorate may be determined by adding to it in solution potassium iodide in known amount and an excess of an arseniate and sulphuric acid, boiling the mixture between definite limits of concentration, determining by titration with iodine the amount of arsenious oxide produced, and calculating the amount of chlorate present, from the difference between the amount of arsenious oxide thus produced and that which should be produced if the whole amount of iodide added were allowed to act upon the arseniate alone. There appears to be no reason why a bromate treated by this process should not leave a similar record of its oxidising power. A mixture of bromate and chlorate should, therefore, in this process, leave a record of the full amount of oxidation of which both together are capable. The following table contains the account of experiments made in this manner upon the sample of bromate, the action of which in the iodide method and in the arsenious acid method is recorded in Tables II. and III.

TABLE IV.

H₂SO₄ (1 : 1), 20 c.m.³; Initial Volume, 105 to 170 c.m.³; Final Volume, 35 c.m.³.

KBrO ₃ taken.	H ₂ KAsO ₄ taken.	I value of KI taken.	Iodine corresponding to As ₂ O ₃ produced.	Iodine corresponding to KBrO ₃ .	Error in terms of KBrO ₃ .
Grm.	Grms.	Grm.	Grm.	Grm.	Grm.
1. 0.0700	2	0.4146	0.0948	0.3198	0.0002+
2. 0.0700	2	0.4146	0.0954	0.3192	0.0000
3. 0.0700	2	0.4146	0.0969	0.3177	0.0003-
4. 0.0700	2	0.4146	0.0975	0.3171	0.0004-
5. 0.1400	2	0.7832	0.1458	0.6374	0.0001-
6. 0.1400	2	0.7832	0.1463	0.6369	0.0002-
7. 0.1400	2	0.7832	0.1462	0.6370	0.0002-

The mean error of these determinations, in which all oxidising material is calculated as bromate, is not far from 0.0001- grm.

TABLE V.

A. Arsenious Acid Method.

Volume not exceeding 100 c.m.³.

KBrO ₃ taken.	As ₂ O ₃ taken.	H ₂ SO ₄ (1:1).	Time.	As ₂ O ₃ unchanged.	As ₂ O ₃ oxidised.	Error in terms of KBrO ₃ .
Grm.	Grm.	Grms.	Mins.	Grm.	Grm.	Grm.
At the Boiling Temperature.						
0.0704	0.2475	5	10	0.1241	0.1234	0.0010-
0.0704	0.2475	5	15	0.1239	0.1236	0.0009-
0.0704	0.2475	5	15	0.1236	0.1239	0.0007-

On the Steam-bath, -80°.

0.0704	0.2475	5	30	0.1241	0.1229	0.0013-
0.0704	0.2475	5	30	0.1246	0.1234	0.0010-

At Atmospheric Temperature.

0.0704	0.2475	5	10	0.2066	0.0409	0.0474-
0.0704	0.2475	5	10	0.1991	0.0488	0.0426-
0.0704	0.2475	5	30	0.1533	0.0922	0.0185-
0.0704	0.2475	5	60	0.1231	0.1244	0.0004-
0.0704	0.2475	5	120	0.1242	0.1233	0.0011-
0.0704	0.2475	5	120	0.1238	0.1237	0.0009-

B. Arseniate-Iodide Method.

H₂SO₄ (1 : 1), 20 c.m.³; Initial Volume, 110 c.m.³; Final Volume, 35 c.m.³.

KBrO ₃ taken.	H ₂ KAsO ₄ taken.	I value of KI taken.	Iodine corresponding to As ₂ O ₃ produced.	Iodine corresponding to KBrO ₃ .	Error in terms of KBrO ₃ .
Grm.	Grms.	Grm.	Grm.	Grm.	Grm.
0.0704	2	0.3812	0.0607	0.3205	0.0001-
0.0704	2	0.3812	0.0588	0.3224	0.0003+
0.0704	2	0.3812	0.0595	0.3217	0.0001+
0.0704	2	0.3812	0.0590	0.3222	0.0002+
0.0704	2	0.3812	0.0615	0.3197	0.0003-
0.0647	2	0.3812	0.0839	0.2973	0.0004+

In the case of still another preparation of potassium bromate, made by acting with commercial bromine on potassium hydroxide, crystallising and re-crystallising several times, determinations by means of arsenious acid, and by the arseniate-iodide process, resulted as shown in Table V.

The mean error of the arseniate-iodide process applied to this particular sample of bromate is 0.0001+ grm. in terms of bromate; the arsenious acid method shows a mean deficiency of about 0.0009 grm. for the smaller amount of bromate employed, if, as is obviously reasonable, those results are omitted from the averages which were obtained by standing at the ordinary temperature for periods less than one hour.

It appears, therefore, that the deficiency in the indications of the iodide process and the arsenious acid process are satisfactorily accounted for by the presence in the bromate of traces of chlorate; and that the oxidising power of a bromate may be determined by boiling it in solution with a known excess of arsenious oxide and an excess of sulphuric acid, and determining the amount of arsenious oxide remaining unchanged. A chlorate, as we have found by direct experiment, is scarcely affected by this treatment.

OUR PRESENT KNOWLEDGE OF AROMATIC DIAZO-COMPOUNDS.*

By GILBERT THOMAS MORGAN, D.Sc., F.I.C.

(Concluded from p. 216).

D. The Diazonium Radicle compared with Quaternary Ammonium Ions.

THE change of opinion in favour of the Strecker-Blomstrand formula for the diazonium salts was in the first place based on certain general analogies existing between the salts of nitrogenous bases.

The older view of the constitution of diazonium salts indicates that these substances form an exception to the rule that basic nitrogen is pentavalent in its salts, and yet the compounds in question behave as the salts of bases, more powerful than the aromatic amines from which they are derived. The diazonium bases are capable of combining with the weaker acids, and yield soluble alkaline carbonates, e.g., (C₆H₅N₂)₂CO₃, and unstable nitrites and acetates. Moreover, this view involves the assumption that the compound C₆H₅N:NOH can react as a strong ammonium base towards acids and as a distinctly acidic substance towards the alkali hydroxides. Hantzsch showed that the diazonium salts of the mineral acids are strongly ionised in dilute solution, but do not exhibit any trace of hydrolytic dissociation; the ionisation is, however, considerably diminished by the introduction of negative radicles into the aromatic nucleus of the diazonium compound (*Ber.*, 1895, xxviii., 1734).

Determinations of the electrical conductivity of solutions of benzene-diazonium chloride and nitrate showed that the benzenediazonium radicle is strictly comparable with other quaternary ammonium ions. The rate of migration of the benzenediazonium ion at 25° is 45.7, the corresponding constants for the methylpyridinium, C₅H₅NCH₃, and tetramethylammonium ions, N(CH₃)₄, being 44.3 and 43.6 respectively.

The molecular conductivity of the solutions of diazonium salts increases with the dilution just as in the case of the corresponding potassium and ammonium compounds.

A physico-chemical study of the solutions of benzene-diazonium hydroxide showed that the affinity constant of this base at 0° is seventy times greater than that of ammonium hydroxide, and somewhat exceeds that of piperidine. The affinity constants of methoxybenzene-

* Report presented to Section B, British Association, Belfast Meeting, 1902.

diazonium hydroxide and ψ -cumidinediazonium hydroxide are even greater, and approximate closely to those of the alkali hydroxides. The effect of introducing halogen radicals into the aromatic nucleus is indicated in a striking manner in the following table:—

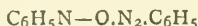
	k =velocity constant.
$\text{C}_6\text{H}_5\text{N}_2\text{OH}$	0.123
$\text{BrC}_6\text{H}_4\text{N}_2\text{OH}$	0.0149
$2:4\text{-Br}_2\text{C}_6\text{H}_3\text{N}_2\text{OH}$	0.0136
$2:4:6\text{-Br}_3\text{C}_6\text{H}_2\text{N}_2\text{OH}$	0.0014

A comparison of the electrical conductivity experiments with the results obtained in the hydrolysis of ethyl acetate by benzenediazonium hydroxide shows that, in 1/128 N solutions at 0°, approximately 33 per cent of the base exists in the ionised condition.

The ionisation detected in the hydrolysis experiment is greater than that indicated by the conductivity determinations, and this shows that the electrolytic dissociation is exclusively due to the reaction—



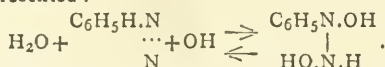
and not to the existence of a diazonium *syn*-diazo-oxide,—



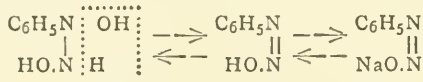
Condition of the Non-ionised Diazonium Hydroxide.—The solution of benzenediazonium hydroxide differs essentially from one containing piperidine in its behaviour towards alkali hydroxides, generating with these reagents an appreciable amount of heat exactly like a weak acid. This reaction is also indicated by determinations of the electrical conductivities of solutions of the diazonium hydroxide when treated with one, two, or molecular proportions of sodium hydroxide.

The simplest explanation of this phenomenon is based on the assumption that the non-ionised portion of the diazonium hydroxide exists in solution in a hydrated form which, on the addition of alkali hydroxide, yields the alkali salt, the acidic *syn*-diazo-hydroxide behaving in this respect precisely like the similarly constituted oximes.

Before the addition of alkali the equilibrium may be thus represented:—

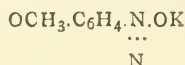


The addition of the alkali hydroxide causes the hydrate to lose water, forming the *syn*-diazo-hydroxide, which then gives rise to a certain amount of sodium derivative,—



(Hantzsch and Davidson, *Ber.*, 1898, xxxi., 1612).

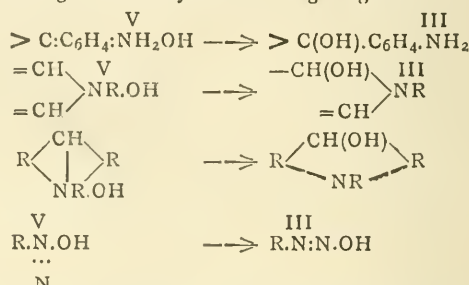
If this hypothesis is not accepted, then it must be assumed that a quaternary ammonium hydroxide, having the functions of a strong base, is also capable of behaving as an acid, and yielding an alkali salt. The diazonium hydroxide derived from anisidine, for example, is a base comparable in strength with the alkalis, and yet it gives rise to a stable potassium derivative (*Ber.*, 1900, xxxiii., 2158), which, according to the alternative theory, has the formula—



There are, however, absolutely no other examples of strong alkalis behaving in this way.

On the other hand, the hypothesis based on the change of configuration due to the labile nature of the diazonium hydroxides, brings these bases into line with other quaternary ammonium derivatives. It is well known that almost all the quaternary ammonium hydroxides, excepting

those in which the nitrogen is attached to four fully saturated hydrocarbon radicals, are unstable, and pass into substances in which the hydroxyl group is no longer attached to the aminic nitrogen. This alteration is noticed in the bases of the rosaniline, pyridine, and acridine series; the transformations taking place in each case being indicated by the following diagrams:—

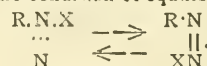


Ammonium derivatives.

Pseudo-ammonium derivatives.

According to this generalisation the *syn*-diazo-hydroxides are to be regarded as pseudo-diazonium derivatives (*Ber.*, 1899, xxxii., 3109; 1900, xxxiii., 278).

Solid Diazonium Halides.—The unstable character of certain diazonium halides seems to be connected in some way with their colour, the most highly coloured salts being very explosive. These coloured salts are found to give colourless solutions, in which the salt is undoubtedly in the form of a diazonium compound. The appearance of colour in the solid state is considered to be due to the formation of a certain amount of *syn*-diazo-derivative, in accordance with the condition of equilibrium:—

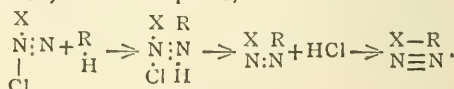


The amount of coloured *syn*-compound present depends largely on the nature of the acid radicle X.

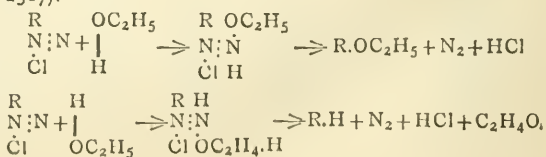
The diazonium chlorides, and nearly all the bromides, are colourless and comparatively stable. The iodides are all coloured, and very explosive, the thiocyanates are somewhat less coloured than the iodides, and are intermediate in stability between these and the bromides.

The influence of substituent radicals in the aromatic radicle R is scarcely noticeable with the diazonium chlorides; but with the other salts it is found that the stability is increased by the introduction of methyl and methoxy groups, and diminished by that of acidic radicals (*Ber.*, 1900, xxxiii., 2179). At low temperatures even the very explosive diazonium salts become stable, and it is noticed that, on cooling, their colour is perceptibly diminished (*Ber.*, 1901, xxxiv., 4166).

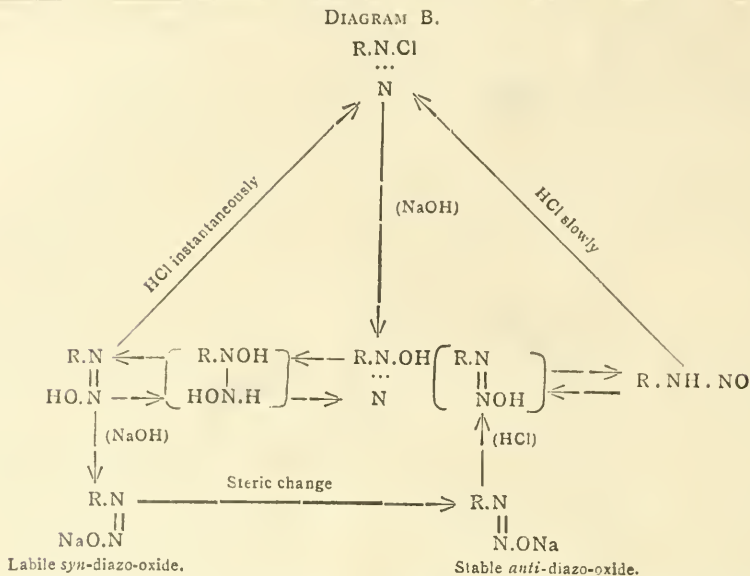
The Residual Affinity of Diazonium Salts (*Ber.*, 1897, xxx., 2548; 1898, xxxi., 2053).—The characteristic fission of diazonium salts is very probably due to the preliminary addition of a reagent HR, and the subsequent elimination of the hydride of the acid radicle with the formation of an unstable *syn*-diazo-compound,—



This hypothesis affords a general explanation of the Sandmeyer reaction, and also of the interaction between diazonium salts and water or alcohol (*Ber.*, 1900, xxxiii., 2517).



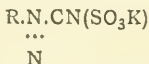
2. They do not indicate that capacity for coupling with



phenols to form azo compounds which is so essentially characteristic of the *syn*-diazo series.

3. Moreover, they involve the additional assumption that the isomerism of the metallic diazo-oxides differs essentially from that of the diazo-cyanides and diazo-sulphonates, inasmuch as the latter compounds cannot be formulated on these lines. This hypothesis is, however, unjustifiable, for the *syn*-diazo derivatives of the three series (oxides, cyanides, and sulphonates) have comparable properties.

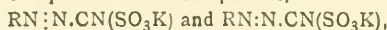
The only other structurally dissimilar formulæ available for the *syn*-diazo-cyanides and diazo-sulphonates are the diazonium formula—



and the configuration $R.N : N.CN(SO_3K)$.

The former of these is not in accordance with the general properties (colour and sparing solubility) of these derivatives, and, moreover, the electrolytic dissociation of the diazo-sulphonates into two ions confirms the view that the compounds are diazo-sulphonates, $R.N:N.SO_3K$, and not diazonium sulphites.

The second formula involves an entirely new assumption—namely, that of isomerism due to change of valency; but even if this possibility be granted, the corresponding formulation does not furnish an explanation of the close relationship existing between the *syn* and *anti* series, for the isomeric pairs of diazo-compounds,—



being derivatives of pentavalent and trivalent nitrogen respectively, ought to differ completely in their chemical reactions.

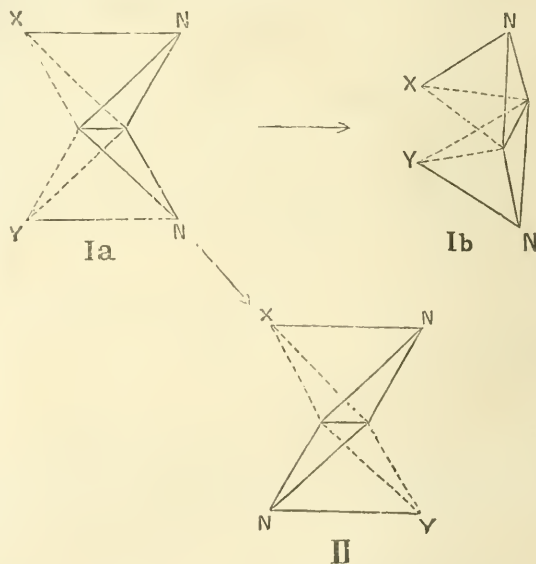
In developing the stereochemical theory of the diazo-derivatives, Hantzsch adopts the space formulæ employed in explaining the isomerism of the oximes.

The assumption involved is that the valencies of the trivalent nitrogen atom are directed along the convergent edges of a regular tetrahedron, the atom itself being situated at the apex of the solid angle thus produced.

When two nitrogen atoms become doubly linked in a molecule, the compound which results is capable of existing in two stereoisomeric forms corresponding with the diagrams Ia and II.

By means of these diagrams the *syn*- and *anti*-diazo derivatives may be compared with the stereoisomeric oximes and the *cis*- and *trans*-isomerides of doubly linked carbon compounds.

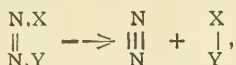
The great instability of the *syn*-diazo series may be explained in terms of v. Baeyer's "tension" theory. According to this hypothesis, the valencies linking together two conjugated atoms tend to set themselves in the same straight line, and when this is not possible, a stress is produced in the molecule which renders it unstable and prone to undergo re-arrangement.



The diagram Ia indicates a molecule in this unstable condition, the linking valencies of the two nitrogen atoms being inclined at an angle to each other. This intramolecular strain can be relieved by placing the sides of the tetrahedra bounded by continuous lines in the same plane, the necessary change in the spatial relationship of these figures being produced either by re-arrangement (Ia to Ib), or more simply by rotating the tetrahedra about their common edge (Ia and Ib).

The former operation represents the transformation of the labile *syn*-derivative into its stable *anti* isomeride; the latter indicates the final condition of the *syn*-com-

pound itself, and furnishes an explanation of the typical diazo-fission,—



brought about by the close proximity of the radicles attached to the diazo-complex.

II. *Isolation of the Anti-diazohydroxides R.N:N.OH.*—Hantzsch has recently discovered that in certain cases both forms of the anti-diazohydroxides are capable of separate existence. The nitrosamine forms have already been studied; they are comparatively stable yellow compounds belonging to the category of pseudo-acids, and yield negative results when treated with phosphorus pentachloride, acetyl-chloride, phenyl-carbimide, or a dry ethereal solution of ammonia.

The newly isolated oxime forms—

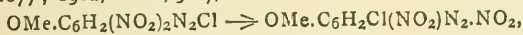


corresponding with the metallic anti-derivatives R.N:NONa(K), are labile colourless substances; they are true acids reacting with the agents enumerated in the preceding sentence.

The syn-diazohydroxides are only known in solution.

III. *Transformation of Diazonium Salts.*—The following observations should be added to the summary of miscellaneous substitutions:—

Meldola and Eyre have shown that in the dinitro-anisidines a nitro-group situated in the ortho- or para-position with respect to amidogen is replaced either by chlorine, when the base is diazotised in the presence of hydrochloric acid (Meldola and Eyre, *Trans.*, 1901, lxxix., 1077; 1902, lxxxi., 988),—



or by hydroxyl, when the operation is carried out in sulphuric acid.

The author has quite recently noticed a similar transformation in the case of α -nitro β -naphthylamine when diazotised in the presence of hydrochloric acid, $\text{NO}_2\text{C}_{10}\text{H}_6\text{N}_2\text{Cl} \longrightarrow \text{Cl.C}_{10}\text{H}_6\text{N}_2\text{NO}_2$, and further rearrangements of this nature have been observed by other investigators (Gaess and Ammelburg, *Ber.*, 1894, xxvii., 2211; Meldola and Streatfeild, *Trans.*, 1895, lxvii., 909; *Fr. Pat.* 315932, February 28, 1902).

Although under these conditions bromine may be replaced by chlorine, it does not appear possible to remove fluorine or iodine from the aromatic nucleus through the agency of the diazo-reaction (Hantzsch).

A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM, AND DIDYMIUM, AND ITS APPLICATION TO THE ANALYSIS OF MONAZITE.*

By FLOYD J. METZGER.

(Continued from p. 219).

Method of Analysis.

MAKE the solution of the neutral nitrate 40 per cent alcohol (volume about 150 to 175 c.c. with 0.1 to 0.2 gm. thorium dioxide and about the same amount of admixed oxides), then add 12 to 15 c.c. of fumaric acid solution (about 0.10 gm. per 10 c.c.) for each 0.1 gm. thorium dioxide, and heat to boiling (75–80° C.); allow to stand a few minutes until the precipitate settles, then filter (while still hot) through a long-stem funnel, or by suction.

* Contribution from the Havemeyer Laboratories, Columbia University. Read at the meeting of the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxiv., No. 10.

TABLE.

CeO ₂ .	La ₂ O ₃ .	Di ₂ O ₃ .	Fumaric acid. C.c.	Volume. C.c.	ThO ₂ .	
					Taken.	Found.
A.						
0'2000	—	—	25	150	0'1725	0'1730
0'2000	—	—	25	150	0'1961	0'1982
—	0'2000	—	25	150	0'1921	0'1941
—	0'2000	—	25	150	0'1961	0'1991
—	0'2000	—	25	150	0'1882	0'1907
—	0'2000	—	25	150	0'1961	0'1978
—	—	0'2000	25	150	0'1961	0'1992
—	—	0'2000	25	150	0'1961	0'1972
—	—	0'2000	25	150	0'1882	0'1901
—	—	0'2000	25	150	0'1961	0'1979
B.						
0'2000	—	—	25	150	0'1961	0'1966
0'2000	—	—	25	150	0'1961	0'1957
—	0'2000	—	25	150	0'1961	0'1964
—	0'2000	—	25	150	0'1961	0'1959
—	—	0'2000	25	150	0'1961	0'1965
—	—	0'2000	25	150	0'1968	0'1965
C.						
0'283	0'133	0'157	10	175	0'0557	0'0558
0'283	0'133	0'157	25	200	0'0572	0'0571
0'283	0'133	0'157	10	175	0'0572	0'0574
0'283	0'133	0'157	10	175	0'0557	0'0558
0'566	0'266	0'314	15	350	0'1115	0'1114
0'566	0'266	0'314	15	350	0'1129	0'1132
D.						
0'1000	0'1000	0'1000	10	120	0'0995	0'0990
0'1000	0'1000	0'1000	10	120	0'1003	0'0995
0'1000	0'1000	0'1000	25	130	0'1529	0'1523
0'1000	0'1000	0'1000	40	150	0'2007	0'2002
0'1000	0'1000	0'1000	40	150	0'2015	0'2010
0'1000	0'1000	0'1000	60	150	0'3011	0'3005
0'1000	0'1000	0'1000	60	150	0'3019	0'3023
0'0500	0'0500	0'0500	25	200	0'1961	0'1963
0'0500	0'0500	0'0500	25	200	0'1968	0'1969
0'0250	0'0250	0'0250	25	200	0'1976	0'1971
0'0250	0'0250	0'0250	25	200	0'1991	0'1985

Wash the precipitate four or five times with hot 40 per cent alcohol, then put paper and precipitate into a platinum crucible, ignite, and weigh as thorium dioxide. A number of analyses were made in this way, using mixtures of thorium with cerium, lanthanum, and didymium, and it was found that the thorium invariably carried with it an appreciable quantity of the impurity which could not be washed out, nor could it be prevented by the addition of such salts as ammonium chloride, ammonium nitrate, &c.

A few results will show the extent to which these impurities are carried down (see Table, A).

Re-precipitation was next tried, and gave very satisfactory results. For this re-precipitation it is only necessary to dissolve the precipitate of thorium fumarate (formed by the first precipitation) off the filter in hot dilute hydrochloric acid—or better, place the paper and precipitate back into the beaker, add a little dilute hydrochloric acid, heat, then filter off the paper—and evaporate to dryness on a water-bath. During the process of this evaporation some of the salt adheres to the sides of the beaker, but this is easily obviated by shaking the beaker occasionally and washing down with a few drops of water from a wash-bottle.

When the residue is free from acid (better add a few cubic centimetres of water and evaporate a second time), add about 50 c.c. water (leaving the beaker on the water-bath) and stir the residue loose from the bottom with a rubber-capped stirring rod; some carbonaceous matter from the fumaric acid, partly decomposed, and also some fumaric acid and a trace of thorium fumarate, will remain insoluble at this point, but need not be regarded. Add

alcohol sufficient to make the solution 40 per cent, dilute to the proper volume with 40 per cent alcohol, add a little fumaric acid (8 to 10 c.c.), and precipitate as before; wash, ignite, and weigh.

Hydrochloric acid was used instead of nitric for the solution of the thorium fumarate, for the reason that nitric acid formed, on evaporation, a deposit which was practically insoluble in water. The accompanying results will show the accuracy of the separation (see Table, B).

Mixtures of thorium, cerium, lanthanum, and didymium were then made in the proportions in which they are usually found in monazite sand, and analysed the same as above, with the results shown (see Table, C).

Mixtures containing equal amounts of thorium, cerium, lanthanum, and didymium, and mixtures containing thorium in excess, were then analysed as shown (see Table, D).

(To be continued).

A NEW LABORATORY SHAKING MACHINE.

By GERALD T. MOODY.

THE machine described is a modification of an "American cream-drink shaker," is very efficient, is inexpensive, and does not get out of order. The glass bottles or other

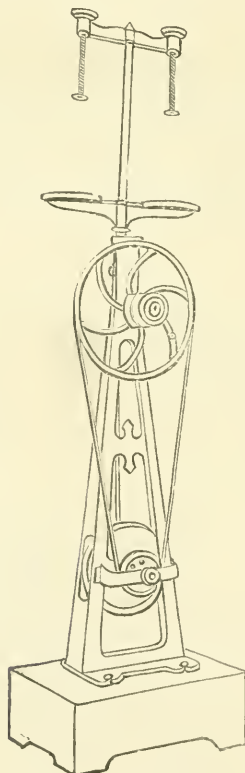


FIG. 1.—Front View.

vessels, the contents of which are to be shaken, are gripped in a frame and given a rapid vertical oscillatory motion.

The machine consists of a cast-iron standard (Figs. 1 and 2), which carries two bored parallel brackets 3 inches apart, and through these passes a vertical working rod. To the top of the rod is attached an iron framework, comprising a central stem to which are fixed, at the lower end, a cast

double bracket on which the bottles, &c., rest, and at the upper end a double bracket carrying tightening screws. This framework and the vertical rod are given vertical motion by means of an iron connecting rod, at the upper end fastened to the working rod by a pin-joint; at the lower end given rotary motion by a crank-pin affixed to a small cast-iron balanced fly-wheel. The fly-wheel is attached by a set screw to a horizontal shaft supported by the iron standard, and carrying a cast-iron V-pulley about 3½ inches in diameter. Motion is transmitted to this pulley by means of an 11½-inch grooved hand-wheel and round leather belt, the hand-wheel running on a fixed horizontal shaft, bolted to the standard, and having vertical adjustment.

To use the machine for shaking, the bottle or other containing vessel is placed on a felt pad on one of the arms of the moving frame, and held down by the tightening screw, between which and the bottle-stopper is placed an indiarubber bung.

At the Central Technical College, where the machine is run by power, a 3" × 1" inch cast-iron pulley is bolted to the hand-wheel, and a similar pulley runs loose on the fixed horizontal shaft, which is considerably longer than the one used with the hand-wheel alone. A 1 inch single strap leather belt transmits power from a 2½-inch gas-engine shaft running at 200 revolutions. The machine then runs at nine complete oscillations per second, which

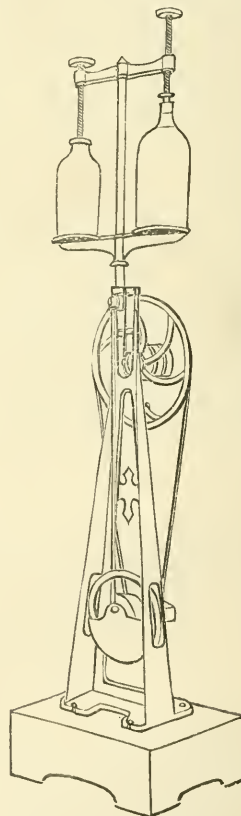


FIG. 2.—Back View.

is very effectual in working. The belt is struck from loose to fast pulley, and *vice versa*, by a striker attached to the fixed shaft.

The machine has been made to specification, and is supplied by Messrs. White, The Eagle Mills, New Church Road, Camberwell.

South Kensington, October 28, 1902.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, October 31st, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

A PAPER "On the Existence of a Relationship between the Spectra of some Elements and the Squares of their Atomic Weights," by Dr. W. M. WATTS, was read by Prof. EVERETT.

The author has detected two kinds of relation between the spectra of some allied elements. In the first kind, which is illustrated by comparisons between zinc, cadmium, and mercury, and also between gallium and indium, the differences between the oscillation frequencies of certain lines of one element, are to the differences between the oscillation frequencies of the corresponding lines of another as the squares of their atomic weights. In the second kind the relation is not between two but between three spectra, and is illustrated by the trio potassium, rubidium, and caesium, as well as by the trio calcium, strontium, and barium. The element of greater atomic weight has the smaller frequency; and, in comparing corresponding lines, one from each of the three spectra, the differences of frequency are proportional to the differences between the squares of the atomic weights. If each of the spectral lines in question is represented by a point whose co-ordinates are "frequency" and "square of atomic weight," the three points which represent three corresponding spectral lines will lie on one straight line in the diagram, and these straight lines will be parallel for all the components of a given set of corresponding groups. When a similar mode of plotting by points is employed to exhibit the first kind of relation, the joins of corresponding points meet in a point, which lies on the axis of frequencies; in other words, on the line of zero atomic weight. This relation was indicated by Ramage about a year ago as holding for corresponding doublets and triplets.

Lord KELVIN expressed his interest in the paper.

Prof. PERRY asked to what extent the points actually lay upon straight lines. He had worked with the spectra of potassium, rubidium, and caesium, and knew that many relations which apparently held, on careful examination were found not to be true on account of certain points falling slightly off the curves. He would like to compare the author's results with some of his own work.

A paper on "The Size of Atoms" was read by Mr. H. V. RIGOUT.

This investigation deals with the size of dissociated atoms, or ions, and the results obtained refer to a dissociated atom, as the smallest quantity of matter which can take part in an electrolytic action. The element chosen is hydrogen, and the author concludes that, in round numbers, $114\frac{1}{2}$ million atoms are necessary to form a line 1 c.m. long. The method employed consists in finding a pair of spheres which would be charged by the quantity of electricity known to be necessary to electrolyse a given quantity of the body under examination—in this case water—to the known difference of potential of its ions. From this the size of the atoms is deduced, subject to certain assumptions enumerated and discussed in the paper. The atoms are regarded as spherical and closely packed. To facilitate the calculations, the packing is assumed to be such that the centre of any sphere is immediately above the centre of the sphere upon which it rests. Under these circumstances the total volume of spheres necessary to fill a given cube is equal to that of the single sphere about which the cube is described. The electrical capacities of isolated spheres being proportional to their diameters, it follows that the total capacity of any number of such spheres is equal to the capacity of a single sphere, the diameter of which is equal to the sum of the diameters of the small spheres. Using these

two propositions, the size of the atoms is easily deduced from the pair of spheres already determined. The author points out that the method fixes both the superior and the inferior size of the atoms, and gives, therefore, the true value.

Lord KELVIN remarked that he had often concerned himself with the size of atoms, and pointed out that the value obtained by the author for the diameter of a hydrogen ion was almost exactly one-half of that which he had obtained for the diameter of a molecule of hydrogen. The fact, however, might be a coincidence. He had dealt with a sphere which would have the same effect as a double atom of hydrogen. While avoiding the assumption that atoms are hard and spherical, it was usual to treat them as such for purposes of calculation. The paper was an important one, but there were many assumptions which required looking into. Lord Kelvin said that in dealing with the subject of atoms, it was necessary to consider the atoms of electricity. The atomic theory of electricity, now almost universally accepted, had been thought of by Faraday and Clerk-Maxwell, and definitely proposed by Helmholtz. The atoms of electricity were very much smaller than the atoms of matter, and permeated freely through the spaces occupied by these greater atoms, and also freely through space not occupied by them. An atom of electricity in the interior of an atom of matter experienced electric force towards the centre of the atom. We were forced to conclude that every kind of matter had electricity in it, and Lorenz had named electricity as the moving thing in atomic vibrations. If the electrions, or atoms of electricity, succeeded in getting out of the atoms of matter, they proceeded with the velocity of light, and the body was radio-active. It was therefore not surprising that some bodies showed radio-active properties, but rather surprising that such properties were not shown by all forms of matter. Our knowledge of this subject, which originated with the discovery of the Becquerel rays, had been greatly advanced by the experiments carried out at the Cavendish Laboratory, and he had no doubt that in the next two or three years much light would be thrown upon this important matter.

Prof. EVERETT asked why the author had taken the specific inductive capacity of water equal to two.

The AUTHOR said that the latest determinations of the constant approximated to that number.

Prof. H. L. CALLENDAR exhibited some Vacuum Calorimeters.

Three of the calorimeters were for the determination of the specific heat of mercury, water, and steam respectively by the steady-flow method. The fourth was a vacuum-jacketed Bunsen calorimeter. Prof. Callendar gave some details of the instruments, and described the method of using them.

Miss A. EVERETT exhibited some Photographs of Cross-Sections of Hollow Pencils formed by Oblique Transmission through an Annulus of a Lens.

The direct rays of an arc light were allowed to pass through an annulus of a convex lens tilted to an angle of 45° with their direction, and placed at a distance of about twice its focal length from the arc. The photographic plate was placed at right angles to the beam, and a series of exposures were made at gradually increasing distances from the lens. Two series of photographs were shown, the first series from a plano-convex lens with one annulus, and the second from a double convex lens with two annuli.

The meeting then adjourned until November 14, 1902.

Essence of Cedar-wood from the Atlas Mountains.—Emilien Grimal.—The author prepares an essence from Atlas cedar-wood, an Algerian variety of cedar of Lebanon, by distillation with water. He examines the properties of this substance, and subjects it to a series of fractional distillations. By this means he isolates a cadinene, $C_{15}H_{24}$, and a ketone, $C_9H_{14}O$, which gives the essence its special odour. It also contains traces of ordinary acetone.—*Comptes Rendus*, cxxxv., No. 15.

NOTICES OF BOOKS.

Chemistry by Observation, Experiment, and Induction. A Laboratory Manual for Students. By J. I. D. HINDS. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1902. Pp. viii.-192. 12mo. Illustrated.

THE author, who is Professor of Chemistry in the University of Nashville, Tennessee, is already favourably known by his larger treatise, "Inorganic Chemistry," issued by the same publishers. The object of the course outlined in this little volume is "to make the student practically familiar with the properties and reactions of the more important chemical elements and compounds, and to lead him by processes of inductive reasoning to the general principles of theoretical chemistry." The book is of necessity elementary and sketchy; the latter feature is prominent owing to the fact that many of its pages consist of questions about properties and reactions, so printed as to leave blank spaces for the answers to be written in by the students. It seems to the reviewer that the book would have been improved by omitting some of the questions to which the answers are so obvious that they (the questions) are really superfluous. For example, after simple instructions how to prepare, collect, and ignite hydrogen, the question follows:—"Does it burn?" On the other hand, answers to many of the questions cannot possibly be found by the students using this volume, as the questions require knowledge gained elsewhere.

Referring again to hydrogen, three lines below the question already cited occurs this one:—"Heat of the flame?" So far as the reviewer can ascertain by examining the book (there is no index), it contains no information enabling a student to answer this query; the term calories does not occur.

A competent teacher would devise appropriate questions spontaneously, an incapable one would not benefit by a mechanical use of those printed.

The question:—"What does the manganese dioxide do?" when it assists in liberating oxygen from potassium chlorate, might test the knowledge of more proficient students than those for whom the book is intended.

The author uses the spelling adopted by the Chemical Section of the A.A.A.S.; "oxid," "chlorin," "sulfur," &c., a system gradually obtaining more and more favour in the United States.

Used in connection with the larger work of Dr. Hinds this little book may be found helpful.

The volume is well printed and generally free from typographical errors, but "glucenum" (p. 154) has slipped past the eyes of the proof-readers. H.C.B.

Text-book of Electro-chemistry. By SVANTE ARRHENIUS. Translated by JOHN McCRAE, Ph.D. London, New York, and Bombay: Longmans, Green, and Co. 1902.

THIS book is based upon a series of lectures delivered at the University of Stockholm in the autumn of 1897. The German translation, from which this English edition has been prepared, contained considerable additions, the text having been brought up-to-date as far as possible. In the initial chapters, which include a short historical sketch, the fundamental principles underlying the subject are carefully and clearly explained. After considering the general laws relating to the boiling- and freezing-points and vapour pressures of solutions, the author passes to the theory of electrolytic dissociation, and the laws regulating the equilibrium between two phases of a heterogeneous system. The last five chapters are occupied with the calculation of electro-motive forces, potential difference, electro-analysis, and the development of heat by the electric current. The treatment of the subject is most able throughout, and nothing but praise can be accorded to the book, which provides a complete course of electro-chemistry for the student who requires a treatise of moderate difficulty. A useful table of literature references is appended.

Übungsbeispiele für die Elektrolytische Darstellung Chemischer Präparate ("Practical Examples of Electrolytic Methods of Preparation of Chemical Substances"). By Dr. KARL ELBS. Halle-a-S.: Wilhelm Knapp. 1902.

IN the preface to this little book the author points out that up to the present time there has been a great scarcity of books dealing exclusively with electro-chemical methods of preparation of chemical substances. Hence he felt that a collection of suitable examples of such methods would supply a want. The book, which follows the lines of the introduction to electro-chemistry worked through by the students in the University laboratory at Giessen, appears to be admirably suited to its purpose. The student is supposed to be familiar with the use of electrical instruments, and methods of taking simple electrical measurements, this portion of the subject being only very briefly treated in the introduction. Half the book is occupied with methods of preparation of organic compounds, classified under the headings of (1) the electrolysis of organic acids; (2) electro-chemical methods of reduction; (3) electro-chemical methods of oxidation. The experiments are exceedingly well selected, and practical working details are given in all cases. The full explanations with structural formulæ leave no stone unturned to aid the student in acquiring a thorough knowledge of the subject.

Introductory Chemistry for Intermediate Schools. By LIONEL M. JONES, B.Sc., A.R.C.Sc. (Lond.). London: Macmillan and Co., Ltd. New York: The Macmillan Co. 1902. Pp. 195.

THE earlier chapters of this book are devoted as much to physical as to chemical work, and are written in an interesting manner so as to hold the attention of the student. In the simple examination of common substances the student is recommended first of all to note all he can detect by the aid of sight and feeling, whether the material is in lumps or powder, glassy and crystalline, or dull and amorphous, &c. Colour, odour, but *not* taste, are also to be noted; such instructions as these will help a boy to observe many things that would otherwise pass unnoticed, and will be of great use in subsequent work. The author has restricted the scope of the book to what may be called the common objects met with, such as chalk, air, water, coal-gas, &c., but has not taken the reader as far as chemical analysis.

At the end of each chapter there is a list of questions to be answered, and numerous practical exercises are given throughout the book.

Aids to the Analysis and Assay of Ores, Metals, Fuels, &c. By J. J. MORGAN, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. 1902. Pp. 105.

As its title indicates, this book is intended for the use of students in practical metallurgy as a laboratory guide. Only the principal well-tried methods of analysis are given, but of these the descriptions will be found to be clear and ample.

Both the wet and dry assay methods are given for all the principal metals and alloys, the latter including silico-spiegel, ferro-tungsten, ferro-aluminum, ferro-nickel, &c., while the analysis of fuels include those in both the solid, liquid, and gaseous forms. The book will be of undoubted help to students.

Royal Institution.—The annual course of Christmas Lectures, specially adapted to young people, at the Royal Institution, will be delivered by Professor H. S. Hele-Shaw, LL.D., F.R.S., Professor of Engineering in University College, Liverpool, whose subject is "Locomotion—on the Earth, through the Water, in the Air." The first lecture will take place on Saturday, December 27, at 3 o'clock, and the remaining lectures will be delivered on December 30, 1902, and on January, 1, 3, 6, and 8, 1903.

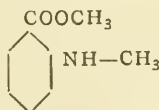
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 15, October 13, 1902.

Pentafluoride of Iodine.—Henri Moissan.—Iodine unites directly with fluorine, the reaction being accompanied by evolution of heat, and the pentavalent compound IF_5 formed. This fluoride possesses great chemical activity. A large number of simple substances decompose it, and in many cases various double reactions take place. When heated to 500° this pentafluoride is decomposed, with evolution of iodine vapour. This phenomenon, however, is only slightly accelerated by an elevation of temperature. The decomposition can be explained either by the fact of a dissociation into fluorine and iodine, or by the presence of free iodine and the production of a new iodine fluoride. The author is continuing his researches on this subject.

Methyl Methylanthranilate in Vegetable Organisms.—Eugene Charabot.—The author's researches lead him to conclude that the essence of the leaves of the mandarine orange tree contains about 50 per cent of methyl methylanthranilate—



Up to the present time appreciable quantities of amido-acid ether have never been discovered in the essential oils. The abundance of methyl methylanthranilate found in one organ like the leaf is of great physiological importance and leads to the conclusion that this body ought to play an interesting part in the process of assimilation of mandarine orange tree.

A New Reaction of Formaline, by which it may be Detected in certain Food-stuffs.—MM. Manget and Marion.—The use of formaline is becoming more and more general for the preserving of food-stuffs, so the efforts of chemists are directed to finding the most susceptible tests for its presence. The most usual method is to act on the product of distillation. The authors' method has the advantage of acting directly and being more sensitive. It is described shortly as follows:—1. *For Milk.*—Lightly powder the surface of the milk with amidol or amidophenol, and leave this for some moments. Normal milk, or that containing boracic acid, develops a salmon colouration; milk containing formaline, a light yellow colouration. This test is sensitive for 1/50,000th part of formaline. 2. *In Meat Jellies.*—Place a little of the liquefied jelly in a tube, and add some crystals of amidol; shake up. If formaline is present, a yellow colouration is produced, turning to a dirty yellow on the addition of a drop of ammonia. When the jelly contains no formaline, a brownish rose-colour is produced, turning to blue under the same conditions.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Brown, Treasurer and Vice-President, in the Chair. The following were elected Members:—Mr. G. H. Baillie, Mr. W. D. Butcher, Mrs. A. R. Cox, Sir Archibald Campbell Lawrie, Mr. G. J. Morrison, and Mr. A. B. Tubini. The special thanks of the Members were returned to Sir Andrew Noble, Bart., K.C.B., F.R.S., for his donation of £150, and to Dr.

Ludwig Mond, F.R.S., for his donation of £200 to the Fund for the Promotion of Experimental Research at Low Temperatures.

Institute of Chemistry of Great Britain and Ireland.—The next Examinations of the Institute of Chemistry, for persons desirous of qualifying themselves to be Public and Technical Analysts, will be held at 30, Bloomsbury Square, London, W.C., in January, 1903. The Examinations are open only to candidates who have complied with the Regulations. The Intermediate Examination will occupy at least four days, commencing on Tuesday, January 6th. Examinations in the following Branches of the Final Examination for the Associateship (A.I.C.) will extend over at least four days, and may commence on either January 6th or 13th:—(a) Mineral Chemistry, (b) Metallurgical Chemistry, (c) Physical Chemistry, (d) Organic Chemistry, and (e) The Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy. (The Final Examination in Branch (f), Biological Chemistry, is held in October each year). Applications for admission to the January Examinations should be forwarded to the Registrar not later than Tuesday, December 2nd, 1902, on which day the List of Candidates will be closed.

Apparatus and Method for Exact Incineration.—H. Wislicenus.—The most satisfactory method for the estimation of the ash of an organic body is that of Wackenroder, viz., incineration in the presence of acetate of lime. This method has the advantage of allowing the complete solution of the ash in hydrochloric acid, and prevents the expulsion of the volatile metalloids by means of the silica or carbon. It is prudent, nevertheless, to add milk of lime to the acetate; this will maintain the excess of alkalinity. The carbonisation is effected easily, but the total combustion of the carbon necessitates the use of certain adjuvants, of which peroxide of hydrogen at 3 per cent is most to be recommended. The material is moistened, dried on the water-bath, and then calcined. The error due to the carrying off of solid particles by the gases and the steam can only be prevented by the help of a special apparatus. That proposed by the author consists of a platinum cover which can be fitted to an ordinary crucible, carrying an escape-tube through which air is drawn. The solid particles carried off by the air are arrested by passing through milk of lime, which is added to the contents of the crucible after the operation. The author recalls another method of calcination which is not very well known, and was devised by Grouven, and which consists in operating in a current of steam between 400° and 700° . The ashes obtained are very pure; they differ from ashes burnt in air, inasmuch as the organic sulphur has disappeared by volatilisation, which is a great advantage in certain cases.—*Zeit. Anal. Ch.*, vol. xl., p. 441.

The Ammoniacal Compounds of Sulphocyanide and of Isosulphocyanide of Copper.—M. Litterscheld.—

Sulphocyanide of ammonia and copper, $\text{Cu} \begin{smallmatrix} \text{NH}_3\text{-CNS} \\ \text{NH}_3\text{-CNS} \end{smallmatrix}$, is obtained in the crystalline form, when dilute solutions of ammonia and sulphocyanide of ammonia are brought into contact with a solution of sulphate of copper. The purified salt gives an analysis corresponding with the above formula. A compound richer in ammonia is obtained when we treat a concentrated solution of sulphate of copper with ammonia at 25 to 30 per cent, in the presence of a sufficient quantity of NH_4CNS . Analysis gives the following formula:— $\text{Cu} \begin{smallmatrix} \text{NH}_3\text{-CNS} \\ \text{NH}_3\text{-CNS} \end{smallmatrix} + 2\text{NH}_3$. The

author has not succeeded in isolating a compound analogous to the isosulphocyanide. It is certainly formed when the isosulphocyanide is heated for a prolonged period with ammonia. In fact, it separates out in beautiful brilliant needles, which cannot be isolated, however, without becoming decomposed rapidly; this fact renders its analysis impossible.—*Arch. d. Pharm.*, vol. ccxxxix., p. 336.

NOTES AND QUERIES.

*. * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Sodium Bismuthate.—(Reply to S. C.)—The preparation is described in the original paper of Reddrop and Ramage, which appeared in the *Transactions* of the Chemical Society, April, 1895, p. 271.—H. GRIPPER, G.C.R., Gorton, Manchester.

Sodium Bismuthate.—S. C. will find the necessary particulars quoted in Breatley and Ibbotson's "Analysis of Steel-works Materials" (Longmans, Green, & Co.).—J. T.

MEETINGS FOR THE WEEK

FRIDAY, 14th.—Physical, 5. "Theory of the Aluminium Electrode." by Dr. W. W. Taylor and J. K. H. Inglis. "Determination of the Ratio of the Specific Heats at Constant Pressure and at Constant Volume for Air and Steam," by W. Makower.

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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2242.

SOME INTERESTING PROBLEMS RELATING TO DAIRY WATER SUPPLIES.

By J. BRISTOWE P. HARRISON, F.I.C.

NOT the least important of the many precautions which are exercised in the control of a large dairy, having the slightest claim to being conducted on the most modern scientific principles, is the regular inspection of the water supplying its many farms, in order to render the risk of contaminating the milk at this stage of its existence as small as possible. In the pursuance of such a system, it is not surprising that some rather interesting—not to say difficult—problems should occasionally present themselves; and in the course of my duties as Assistant Chemist to the Aylesbury Dairy Co., Ltd., it has occurred to me, on more than one occasion, that some of the more difficult problems relating to the supplies of that Company's various farms might be of sufficient interest to dairy chemists, public analysts, and others interested in water analysis to justify their publication.*

For the purposes of this paper, I shall denote the examples mentioned as A, B, C, &c. The time of analysis is placed at the head of each set of results, which are expressed in parts per 100,000.

A common idea which prevails with the owner of a water supply is that once a water is analysed and found to be good, its composition will remain the same to the end of all time. It is only with very great difficulty that you can convince him of the necessity for regular examination, in order to make sure that his supply is proof against contaminating influences.

The results obtained from the analyses of the supplies A, B, and C show how such a water may change in character from time to time, and how imperative it is that the report of the expert should be guardedly expressed when giving his opinion as to the quality of a supply for the first time.

"A" is a well about 60 feet deep to the surface of the water, and apparently far removed from possible sources of pollution. From the results of the first analysis (June, 1896) the water was considered satisfactory, but on re-examination there was distinct evidence of surface pollution. After due precautions had been taken to prevent surface leakage, the water appeared to be changing in character, and its use had to be finally prohibited. It will be noticed that the chlorine figure is high during the year 1899, which was remarkable for its dry summer, and that, while the chlorine increases slightly, in other respects the composition of the water improves. After a very careful consideration of the results obtained at different times, it was concluded that the well was probably supplied by water from at least two different strata—one low in chlorine, the other very high. The low chlorine water is probably the upper one, and in seasons of drought may become exhausted, when the well is fed by the lower supply, mixed with polluting matter which has percolated through the cracked stratum.

The supply "B" is a well about 30 feet deep, and was at first reported as far removed from possible sources of pollution. As the water was constantly varying its composition, a further inspection of the surroundings was made, and revealed the presence of a cesspool. The well was opened, and it was found that the sides were quite

pervious, and therefore liable at any time to let in surface pollution.

"C" was a new well 50 feet deep, and sunk through a layer of rock. To all appearances it was admirably placed, and water was pumped out until the composition of the supply was practically constant, as indicated by the analysis headed November, 1900. The water, for the time being, although rather high in sulphates, was considered satisfactory. Unfortunately, on standing, however, its composition was again found to be unfavourable, owing, no doubt, to the leakage through of surface water, which had accumulated above the solid rock in the loose sub-soil.

Notwithstanding the rapid progress that has been made of late years in other departments of engineering, the well-sinker in the country has still his own ideas as to how a well should be constructed. It is apparently a matter of indifference to him how deep it should be, and at what part of the well the water should enter. He also seems to have a kind of impression that the nearer the well is to some inhabited dwelling, the more convenient it will be for those who use it. The result of all this is that wells are generally sunk in close proximity to inhabited houses, with their defective drains, privies, and cesspools, and impurities from these sooner or later find their way into the water supply. No wonder, then, that so many country wells contain impure water, which are obviously liable at any time to be a source of danger to the public health.

A perusal of the analyses of the supplies D, E, and F will at once make plain that an ideal well should be sunk as deeply as possible and at some considerable distance from any source of pollution, and should also be protected from surface leakage by an impervious stratum. D and E are proximate wells on opposite sides of a road, and undoubtedly fed by the same water, whereas F is a supply altogether distinct from these.

The tube-well "D" is 30 feet deep and reasonably removed from anything which may contaminate it; it penetrates 3 feet into the chalk. From August, 1898, to April, 1902, the water from this well was analysed no fewer than ten times, and its analysis remained almost constant during the whole of that period.

"E" is about 20 feet deep, and situated at the upper corner of a farm-yard at a somewhat lower level than "D." Since it was first analysed it has been constantly changing its composition, but this change has been so small and has taken place so slowly that, so far as the chemical analysis was concerned, the first indications of pollution might have been entirely overlooked if the composition of the supply "D" had not been available as a standard to judge from.

The nitric acid of these two supplies is undoubtedly derived from the chalk. We have here an excellent illustration in which a bacteriological examination is of more value in indicating pollution than a chemical one. The chief point to notice, however, is that one of these supplies being a tube-well and dipping well into the chalk, is rendered impervious to contamination, while the other, standing in the corner of the farm-yard, is always liable to slight leakage.

The supply "F" was thus described:—"The water emerges from a sand spring not far from the top of a hill. It is collected and conveyed by iron pipes through a wood down the side of the hill to a closed reservoir at the bottom. There appears to be no possibility of pollution once it reaches the reservoir."

Such conditions would usually be considered ideal for a water supply, and seeing that it had previously been analysed and reported as pure, it was somewhat of a puzzle to find that on each occasion when the water was examined, the analysis invariably turned out unfavourable. An inspection of the locality by the chemist, however, revealed that a village was situated on the brow of the hill, and that the sand-spring was fed by a number of small brooks which skirted the village. Remembering that the water from the spring was practically surface water, it

* As the features of a good water are of little interest from a scientific point of view, it is hardly necessary to point out that I have purposely chosen for example supplies which were polluted, and the use of which was, of course, prohibited.

A.						
	June, 1896.	May, 1899.	June, 1899.	August, 1899.	March, 1900.	May, 1901.
Chlorine	1'25	22'10	22'90	23'50	22'9	1'45
Free ammonia	0'003	0'0045	0'005	0'008	0'0095	0'004
Albumenoid ammonia	0'005	0'047	0'0145	0'010	0'017	0'0085
Nitrates	1'0	3'8	1'9	None	2'5	0'8
Nitrites	None	None	None	None	Trace	None
Oxygen absorbed in four hours	0'022	0'118	0'135	0'140	0'120	0'019
Phosphates	Trace	Trace	Trace	Trace	Trace	Trace

Bacteriological Examination.

Gelatin culture at 22°, colonies per c.c.	—	3640	—	1310	50	—
Agar culture at 37°, colonies per c.c...	—	Plate covered in 48 hours.	—	3	4	—

B.					
	September, 1897.	November, 1898.	April, 1899.	July, 1899.	October, 1899.
Chlorine	4'1	4'7	4'8	6'0	4'75
Free ammonia	0'001	0'004	Trace	None	None
Albumenoid ammonia	0'006	0'033	0'0195	0'009	0'011
N ₂ O ₅	None	1'2	2'2	1'1	0'2
N ₂ O ₃	None	None	None	None	None
Oxygen absorbed in four hours	0'032	0'057	0'039	0'046	0'042
P ₂ O ₅	None	None	Trace	Trace	Trace

Bacteriological Examination.

Gelatin culture at 22°, colonies per c.c.	—	620	1260	—	Plate covered,
Agar culture at 37°, colonies per c.c...	—	88	42	—	240

C.					
	April, 1900.	May, 1900.	June, 1900.	November, 1900.	April, 1901.
Chlorine	1'9	2'4	1'9	1'9	2'35
Free ammonia	0'0065	0'008	None	0'0045	0'0045
Albumenoid ammonia	0'0095	0'013	0'009	0'007	0'0115
N ₂ O ₅	None	Trace	None	None	0'75
N ₂ O ₃	None	None	None	None	None
Oxygen absorbed in four hours	0'027	0'009	0'131	0'021	0'065
SO ₃	32'4	62'4	53'0	49'4	42'0
P ₂ O ₅	Trace	—	—	—	—

Bacteriological Examination.

Gelatin culture at 22°, colonies per c.c.	—	950	—	240	12,360
Agar culture at 37°, colonies per c.c...	—	5	—	None	4

D.						
	August, 1897.	Sept., 1897.	Nov., 1898.	Nov., 1899.	Nov., 1901.	May, 1902.
Chlorine	1'35	1'35	1'3	1'35	1'35	1'30
Free ammonia	0'002	None	0'0045	None	None	None
Albumenoid ammonia	0'005	0'002	0'004	0'004	0'005	0'0045
N ₂ O ₅	2'0	2'1	2'8	1'8	2'0	1'8
N ₂ O ₃	None	None	None	None	None	None
Oxygen absorbed in four hours	0'018	0'007	None	0'007	0'003	0'015
P ₂ O ₅	None	None	None	None	—	—

Bacteriological Examination.

Gelatin culture at 22°, colonies per c.c.	—	—	None	350	10	530
Agar culture at 37°, colonies per c.c...	—	—	None	1	1	None

E.						
	August, 1893.	Sept., 1897.	Nov., 1898.	Nov., 1899.	Nov., 1901.	May, 1902.
Chlorine	1'35	1'5	1'55	1'5	1'55	1'5
Free ammonia	0'003	0'005	0'003	Trace	0'003	None
Albumenoid ammonia	0'005	0'005	0'0045	0'0055	0'005	0'0065
N ₂ O ₅	2'0	2'1	2'8	2'3	2'0	1'9
N ₂ O ₃	None	None	None	None	None	None
Oxygen absorbed in four hours	0'002	0'027	0'0335	0'028	0'021	0'032
P ₂ O ₅	None	Trace	Trace	Trace	—	—

Bacteriological Examination.

Gelatin culture at 22°, colonies per c.c.	—	—	280	7480	1670	Large
Agar culture at 37°, colonies per c.c...	—	—	Plate covered in two days by <i>B. ramosus</i> .			

Chlorine	3'45
Free ammonia	0'0031
Albumenoid ammonia	0'0130
N ₂ O ₅	7'1
N ₂ O ₃	None
Oxygen absorbed in four hours	0'05
P ₂ O ₅	Trace

F.

Bacteriological Examination.

Gelatin culture at 22°, colonies per c.c.	120
Agar culture at 37°, colonies per c.c.	Whole plate covered in less than 24 hours.

G.

	November, 1896.	November, 1897.	May, 1899.	March, 1900.	November, 1901.
Chlorine	0'95	1'20	1'20	1'20	1'20
Free ammonia	0'002	0'003	0'0025	None	0'002
Albumenoid ammonia	0'010	0'014	0'0145	0'010	0'008
N ₂ O ₅	1'5	1'5	1'2	1'5	0'85
N ₂ O ₃	None	None	None	None	Trace
Oxygen absorbed in four hours	0'016	0'053	0'028	0'013	0'030
P ₂ O ₅	Trace	Trace	None	—	—

Bacteriological Examination.

Gelatin culture at 22°, colonies per c.c.	—	6620	3340	2000	840
Agar culture at 37°, colonies per c.c.	—	None	<i>B. ramosus</i>	<i>B. ramosus</i>	43
Phenol agar culture at 37°, colonies per c.c.	—	None	—	—	—

H.

Free ammonia	0'040	Magnesium sulphate	48'00
Albumenoid ammonia	0'010	Sodium sulphate	268'19
Oxygen absorbed in four hours	0'170	Sodium chloride	49'96
Calcium nitrate	3'04	Potassium chloride	30'85
Calcium carbonate	52'41	Silica	2'10
Calcium sulphate	35'41		

was not very difficult to understand where the pollution was coming from.

This water was analysed four times, and though the analyses varied slightly at each examination, the general character of the water showed no appreciable change. There is evidently no object in recording each separate analysis, so I give the mean of four analyses (see F).

A village with no satisfactory water supply in its own immediate neighbourhood, notwithstanding the many attempts to obtain one by sinking wells, is compelled to cart water from a well on a hill 2½ miles away to obtain a pure water supply. The locality of the well has been thoroughly inspected; the gathering ground is entirely uninhabited, and there is no reason to believe that the supply is other than a good one. The analyses of "G" are a series of examinations of this water which has been carted away in an open tank. For reasons which need not here be considered, it was necessary to analyse this water as received at the village, and not as taken directly at the source. In quoting the following analyses I would specially draw attention to the unfavourable bacteriological indications, which are undoubtedly due to *what the water received on its journey in the open tank*, and not to impurities in the water as taken from the well. Under such circumstances, it is hardly necessary to point out how misleading such indications would be if considered from an absolute standpoint.

The following case is interesting, yet hardly credible in these days of stern fact. It serves to show, however, what a remarkable influence the water finder and his magic rod still have upon the unsuspecting British farmer:—A certain farmer, after spending a considerable sum of money in vain attempts to find a satisfactory water supply, succumbed to the assurances of a water finder who possessed a considerable reputation. They accordingly set out on their mission, and had not gone very far before the farmer reminded his companion, that they had just passed over water. "Yes," replied the finder, "but it is not good water; what I undertake to discover is a good potable water; the divining-rod will not indicate the presence of bad water." The farmer having remarked that the water they had just passed over was "brackish,"

they pursued their course until the hazel-twig "divined" what the finder considered a good potable water. I give the analysis of this (see H); its composition agrees so closely with that of the "brackish" water that there can be no question about their being one and the same. *Verbum sap.*

THE ESTIMATION OF ALCOHOL IN VERY DILUTE SOLUTIONS.

By G. ARGENSON.

THE method I am about to describe enables us to estimate ethylic alcohol in solutions containing only 1 part in 1,000,000 by volume. The principle of the method is as follows:—The alcoholic solution (very dilute of course), of which we wish to know the strength, is treated with chromic mixture and distilled; under suitable conditions the greater part of the alcohol is oxidised to the form of aldehyde, which is found in the first portions which come over on distillation.

If we add a few drops of an aqueous solution of fuchsin, decolourised by sulphurous acid, to the distillate, a violet colouration is obtained, the intensity of which depends on the amount of aldehyde contained in the liquid, and, consequently, on the amount of alcohol in the original solution. As this colouration is very similar to that of dilute solutions of permanganate of potassium, its intensity is estimated in the following manner:—

To a known volume of water, a titrated solution of permanganate is added, drop by drop, until the colouration obtained is of the same intensity as that of the solution under examination; from the volume of the solution of permanganate used we can calculate the amount of alcohol present, by means of preliminary trials on solutions of known strength.

The sensitiveness of this method depends on that of the reagent used; to obtain the greatest delicacy it is best to proceed in the following manner:—Twenty-five grms. of fuchsin are dissolved in a little less than 500 c.c. of water, from which all the dissolved air has been driven off

by boiling; the solution takes place more rapidly in hot than in cold water; after cooling, the volume is made up to 500 c.c., and a very slow current of sulphurous anhydride is passed through; the current of gas is stopped before the decoloration is complete, as the action still goes on with the lapse of time. After a few hours, if the solution is still coloured, a few more bubbles of gas are passed through, and we wait again for a few hours longer, and so on, taking care to stop while the solution still has a faint rose tint. If the operation was pushed further, we should obtain a straw-coloured solution, the sensitiveness of which would be considerably less. When prepared in this manner and used as I am about to show, this reagent will give an appreciable colouration with a solution containing 1 part of alcohol per 10,000,000 by volume.

This reagent will remain intact for several months, if kept in full bottles away from the light.

The reagent made, we do a preliminary determination by operating on a solution of alcohol of known strength, 1 in 500,000 by volume, for example.

For this purpose, we take 20 c.c. of this solution and place it in a flask; 5 c.c. of a saturated solution of bichromate of potassium, and 1 c.c. of concentrated boiled sulphuric acid are added. The flask is placed in communication with a small Liebig's condenser by means of an elbow tube, of which the vertical portion has two or three bulbs blown in it to arrest any projections during distillation; this must be conducted slowly, and always in the same manner. The first 5 c.c. are collected in a test-tube A, marked at this point, and 0.5 c.c. of the reagent is added. The colouration appears gradually, and after about an hour it may be considered permanent. This is the moment for making the comparison of the tint, which is carried out as follows:—Five c.c. of water are placed in a test-tube of the same diameter as the graduated one; then, by means of a small burette, we add a centinormal solution of permanganate, first drop by drop, and then by fractions of a drop, until the colouration is of the same intensity as that in the tube A. The two tubes are compared by transmitted light in front of a sheet of ground glass or oiled paper, and the volume of the solution of permanganate is noted.

The same series of operations is repeated on the liquid in which we wish to know the proportion of alcohol; this latter is practically proportional to the volume of the solution of permanganate necessary to obtain equal tints, for proportions of alcohol comprised between 1 part in 200,000 and 1 part in 100,000 under the conditions described. In many cases, knowing how extremely dilute the solutions under examination are, we may be content with the approximation obtained by applying the rule of proportions, although the relative error may be as great as one-third. If we wish for a closer approximation, the experiment can be repeated with a solution of a strength more closely resembling it than the one first used, and the new figure expressing the volume of the permanganate will serve to correct the first; the relative proportion of this to the volume of alcohol present may be looked upon as correct for solutions of about the same composition.

In the case of solutions containing more than 1 part of alcohol in 200,000 by volume, the reagent will give a colouration of an intensity equal to, or greater than, that of the centinormal solution of permanganate. In such a case the experiment must be repeated after having diluted the solution to a known extent, to bring it within convenient limits.

The centinormal solution of permanganate should be prepared at the time it is required for use; it is advisable to use a burette of very small diameter reading to 1/100th of a c.c.

We may have occasion to estimate the alcohol in a solution which also contains aldehyde; this must be verified by means of the reagent before treating it with the chromic mixture; this aldehyde, added to that formed by the oxidation of the alcohol, would give too high a figure.

The cause of error must be allowed for by distilling 20 c.c. of the solution without treating it with the chromic mixture and continuing the operation as described above. The volume of the permanganate solution must be deducted from that found by the first operation, and the difference will give the figure corresponding to the alcohol only.

We may remark here that alcohol generally contains traces of aldehyde which sometimes give a very intense colouration. I have tried, but without success, to eliminate these traces by acting on the alcohol for a long time with ammoniacal nitrate of silver, potash, and baryta. I have also tried to obtain alcohol free from aldehyde by saponifying, by means of dilute sulphuric acid, the sulphovinate of soda dried by keeping in the oven for several days, taking care to do the saponification in an apparatus from which all the air has been driven by means of a current of carbonic acid.

As a general rule, the amount of aldehyde is sufficiently small for the very dilute solutions used for titrating not to give any appreciable colouration with the most sensitive reagent; this is quite pure enough for ordinary practice.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 18.

"FIXING" NITROGEN FROM THE ATMOSPHERE.

ONE of the first results of Sir William Crookes's Presidential Address to the British Association, in the year 1898, was a feeling of scepticism, followed by alarm, as to the serious extent to which the world's wheat supply is threatened by the failing fertility of the available soil. The principal object of that Address was overlooked by most of its critics, viz., to point out how the threatened failure of the wheat supply could be averted. It was not recognised at that time that this feeling of alarm for the future was emphasised in order to lead up to the remedy which Sir William Crookes had to propose, viz., to augment the supply of nitrates for manurial purposes by the fixation of the atmospheric nitrogen by means of electricity. Fortunately, however, the matter was not lost sight of, and we read now in a paper on this subject by Mr. T. C. Martin, in the September number of *The American Monthly Review of Reviews*, that the manufacture of nitrates from the nitrogen of the atmosphere is in a fair way to become a commercial fact.

It was calculated that in about thirty years' time some 12,000,000 tons of nitrate of soda would be required annually to raise the necessary supply of wheat. The nitrate deposits in Chili are swiftly running out, and the amount now in sight and available is estimated to be good for only fifty years at the present rate of consumption. Hence, even if famine does not impend immediately, the food problem is far more serious than is generally supposed.

Dealing with the conditions as they are, Sir William Crookes pointed to an inexhaustible supply of nitrogen which has now been tapped by the method we are about to describe.

This new industrial enterprise has been founded at Niagara Falls by Messrs. Charles S. Bradley and D. R. Lovejoy, and the method which they have devised consists mainly in the production of a large number of electric arcs or flames in a confined space, through which a regulated amount of air to be burned could be passed continuously; this air emerging from the apparatus laden with nitric oxides, as the result of combustion, is ready for treatment and collection.

A great deal of time and money had to be spent in determining the form or variety of arc that would effect the maximum chemical union of the nitrogen and oxygen in the air. The curious discovery was made at an early stage that "static" sparks, such as are caused by frictional machines, are of very little use for this work; in

fact, there was not enough energy in them. Turning, therefore, to dynamic electricity, the two inventors ascertained that for their work, an alternating current arc was not so good as the direct current arc, and a dynamo was specially wound, giving a direct current at a pressure of 10,000 volts, the power being obtained from Niagara.

The nitrifying chamber in which the arcs are situated consists essentially of a large box of metal, six feet high and three feet in diameter; inside, there is a revolving cylinder or hollow shaft. The box has openings to admit and circulate the air, and all round the walls are rows of fixed electrical contacts for arcing points, arranged in six rows of twenty-three each, or 138 in all. The positive pole of the dynamo is connected in "multiple" or "parallel" to these points, with an induction coil in each circuit so as to prevent the arcs from "short-circuiting" and burning out the dynamo.

The negative pole of the dynamo is connected with the revolving member inside the chamber; this cylinder having contact projections, or wire fingers, corresponding to the contacts on the inside of the box, so that as it spins round, the currents from the 10,000 volt dynamo cross in the air between the stationary contact points and the revolving ones. The arcs are thus rapidly made, broken, and re-made within the chamber. A motor at the top of the apparatus drives the cylinder at a speed of from 300 to 500 revolutions per minute, while air is forced into the chamber at the rate of 5 cubic feet per arc contact per hour. The air leaves the chamber after this treatment laden with $2\frac{1}{2}$ per cent of oxides of nitrogen. The points of contact on the barrel are set each a little in advance of the next so as to form spirals from the top to the bottom of the shaft, enabling the arcs to work on the air without cessation. The arcs themselves are six or eight inches long, which is very much longer than the arc usually used for lighting purposes. From this chamber the acted on air is led away to an absorption tower of the kind generally used in chemical processes, the result of this treatment being nitric and nitrous acids. If the gases are brought into contact with potash, saltpetre is formed; if the base is caustic soda, nitrate of soda is formed.

A careful investigation of this process has shown that, with current at Niagara costing £4 per kilowatt—i.e., 1½ horse-power—per year, the expense for the energy required would be a little less than ¾d. per pound of 70 per cent nitric acid, which is the customary commercial strength of acid selling at 2½d. per pound. There is every reason to believe that this process will be the means of placing a large supply of nitrate of soda on the market, and thus show that science, while continually increasing our wants by facilitating intercommunication, is also able to help humanity out of a great difficulty.

ALLOYS OF CADMIUM AND MAGNESIUM.

By O. BOUDOUARD.

IN two previous papers (*Bull. Soc. Chim.*, Series 3, vol. xxvii., pp. 5 and 45) I described the alloys of aluminium and magnesium from the point of view of their fusibility, and I also described the definite compounds formed by these metals. I have followed up these researches relating to the alloys of magnesium by the examination of those formed with cadmium.*

Fusibility.—Knowing the low melting-point of cadmium, I was able to use, for the purpose of studying the fusibility of the alloys of cadmium and magnesium, a similar process to that which I described in connection with the

alloys of aluminium and magnesium. The following results were obtained:—

Cd per cent by weight.	Mg per cent by weight.	Temperature.
100	—	320°
90	10	410
85	15	500
80	20	440
75	25	400
70	30	480
60	40	525
55	45	505
50	50	560
40	60	575
30	70	590
20	80	635
10	90	650
—	100	635

If we construct a curve, taking the proportions by weight of magnesium as abscissæ, and the temperatures as ordinates, we observe that this curve has three maxima (500, 565, and 650°) and two minima (400 and 560°). The last maximum shows that the corresponding compound is less fusible than either of its two constituents.

Similar facts have already been observed by Sir Wm. Roberts-Austen (gold-aluminium), H. Gautier (antimony-aluminium), and Lebeau (antimony-lithium). These three maxima are evidence of the existence of three definite compounds, CdMg, CdMg₄, and CdMg₃₀.

The alloys of cadmium and magnesium are of a more or less brilliant white appearance; they are easily filed, and are fairly soft; when it is wished to prepare the surface for microscopical examination it is difficult to obtain a perfect polish. From the point of view of malleability the alloys of cadmium and magnesium break when they are submitted to continuous hammering; those alloys containing equal parts of cadmium and magnesium behave the best. We may here remark that this property is the reverse of that observed with alloys of aluminium, and with those of copper which we are now investigating; in the latter case especially the fragility of the metals obtained is very great.

Alloys of cadmium and magnesium preserved in stoppered flasks do not undergo any sensible change in the air. The same is not the case in the presence of water; ingots containing 90 parts of cadmium and 10 of magnesium, 50 cadmium, 50 magnesium, and 10 cadmium, 90 magnesium, are attacked during polishing with a moist cloth impregnated with oxide of iron.

Microscopic Metallography.—The preparation of polished surfaces of the different alloys examined offers difficulties due to their want of hardness; it is difficult, not to say impossible, to obtain a perfect polish. Sometimes besides the softness, we are also troubled with the facility with which the alloys are attacked by water.

The methods of etching are extremely various. In a general way, the mineral acids, even when very dilute (up to 1 per cent), act very energetically in a very short time, and to the attack proper is added a superficial oxidation which makes the photographic reproduction very difficult.

However, by partially re-polishing the polished surfaces thus etched we can obtain satisfactory results. Hydrochlorate of ammonium gave me some good results with alloys of magnesium and aluminium; the same was not the case with those of cadmium and magnesium. Etching by means of the electric current was tried with success.

By varying the proportions of magnesium from 0 to 100, I prepared a series of nine specimens which were examined with a Le Chatelier microscope.

Nitric acid at 5 per cent showed the existence of magnificent dendrites of several millimetres in length in the specimen of 90 cadmium, 10 magnesium; they were even visible to the naked eye (compound CdMg); to obtain a photograph it was only necessary to partially polish the specimen thus etched. By simple polishing in bas-relief

* Parkinson, in his work on the alloys of magnesium, shows that on melting cadmium with 10 per cent of magnesium in a current of hydrogen, he obtained a brilliant silver-white metal as hard as as brittle as magnesium, and coarsely crystalline. This metal tarnishes rapidly; after being kept for three months in a sealed tube, it becomes disintegrated (*Chem. Soc.*, Series 2, vol. v., p. 117).

on a moist cloth, the ingot 50 cadmium, 50 magnesium, shows a very distinct crystallisation (compound CdMg_4). Finally, if after polishing the sample 10 cadmium, 90 magnesium, we wash it in water, we obtain very irregular polygonal contours, which become more distinct by treating with 10 per cent chloride of sodium, under the influence of the electric current (compound CdMg_{30}).

Definite Compounds.—I found it difficult to isolate the definite compounds of cadmium and magnesium. The mineral acids used varied in concentration from 20 per cent to 1 per cent; the acetic acid was at 10 per cent, and the hydrochlorate of ammonium at 10 per cent, but none of these gave me any satisfactory results with the compounds CdMg and CdMg_4 .

1st. CdMg .—The centesimal composition of this alloy corresponds to 82.1 of cadmium and 17.9 of magnesium. If the metallic ingot of 25Mg—75Cd is attacked by 1 per cent hydrochlorate of ammonium in the cold, gas is given off, and, at the same time, a crystalline powder of a grey metallic appearance separates; this is collected, and gives on analysis: Cd = 81.2, 83.3; Mg = 18.7, 17.0.

2nd. CdMg_4 .—The centesimal composition of this alloy corresponds to 53.5 of cadmium and 46.5 of magnesium.

The best method for isolating the compound CdMg_4 consists in treating the metallic ingot of 50Cd—50Mg by means of 1 per cent hydrochlorate of ammonium. The attack can be carried out either hot or cold, and a crystalline powder is obtained. Analysis gives the following results: Cd = 54.8, 51.0, 53.5, 52.65; Mg = 45.3, 48.8, 46.4, and 47.25.

3rd. CdMg_{30} .—The theoretical centesimal composition of this alloy corresponds to 13.2 cadmium and 86.8 magnesium.

All efforts to isolate the compound CdMg_{30} have been unsuccessful; the results given by analysis have varied considerably according to the method of attack adopted.

I. Attack of the ingot 90Mg—10Cd by AmCl at 1 per cent	37.8, 62.1
II. Attack of the ingot 90Mg—10Cd by AmCl at 1 per cent	26.4, 73.1
III. Attack of the ingot 90Mg—10Cd by AmCl at 10 per cent	98.0, 2.0
IV. Attack of the ingot 70Mg—30Cd by HCl at 5 per cent	64.7, 35.3
V. Attack of the ingot 70Mg—30Cd by HCl at 5 per cent	59.6, 40.3

The apparition of the maximum point in the curve of fusibility may be explained by admitting the existence of solid solutions, either between the cadmium and magnesium, or between the definite compound CdMg_4 and magnesium.

The analyses I. and II. verify this latter hypothesis; they correspond to the compound CdMg_4 in an excess of magnesium. As for the analyses III., IV., and V., they indicate that through the too great energy of the reagents used, a large quantity of magnesium has gone into solution. Finally, the micrographic examination of the ingot 90Mg—10Cd has put in evidence a series of irregular polygonal grains which should be thus constituted, not by an individual chemical compound, but by a solid solution. Facts similar to these have been observed with alloys of copper and antimony; the results obtained by M. Le Chatelier in the examination of the fusibility and dilation of these alloys, those of Mr. Stead from the micrographic point of view, and those of M. Kamensky relative to the electrical resistance, establish in fact, the existence of a solid solution in the alloys of copper and antimony.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 16.

Pulegenic Acid.—L. Bouveault and L. Tétty.—The authors have repeated M. Wallach's experiments of obtaining pulegenic acid by the reaction of alcoholate of soda on bibromide of pulegon, but they found that, besides this acid, other interesting products are formed.—*Bull. Soc. Chim.*, Series 3, xxvii., No. 8.

ON THE RAMIE (*BOEHMERIA*) PLANT AND CROP.

By R. W. EMERSON MACIVOR, F.I.C., &c.,
Formerly Assistant Professor of Chemistry, Anderson's College
(Medical Faculty), Glasgow; Consulting Chemist to the National
(now Royal) Agricultural Society, Victoria, Australia, &c.

RAMIE is the bast fibre of several varieties of the genus *Boehmeria* (*Urticaceæ*), but ordinarily of the *B. nivea*. The demand for this valuable material is rapidly increasing year by year, particularly in France and Germany, and must sooner or later cause the cultivation of the crop to extend in every country where the climate, soil, labour conditions, and other circumstances are at all favourable to the industry. It is much to be regretted that we are so far behind our Continental friends in regard to this important textile. The difficulty our manufacturers have hitherto had in obtaining constant and abundant supplies of the raw material has, I am informed, prevented the general adoption of ramie spinning in this country. No doubt when this fact becomes more generally realised by our colonial patriots in the languishing West Indian Islands, Fiji, and other tropical possessions, and substantial prospects are held out to them in the matter of steady markets for their produce, we may hope that they will enter upon the general cultivation of the crop, with incalculable advantage to their respective countries and the whole Empire.

The progress of ramie growing was for many years delayed through the lack of proper means of stripping the fibre-containing bark from the underlying useless wood of the stalk. This difficulty has, however, been overcome, and the bark is sent into the market in the form of "ribbons," or "brown" ramie or rhea. In order to free the fibre from the so-called "gum," pectic, and other substances with which it is naturally associated, the ribbons are subjected to the operation known as "de-gumming." The processes which have been proposed to effect this end are very numerous, and the greater number of them involve the exposure of the ribbons to heated alkaline solutions (usually caustic soda) and acid baths of one description and another for periods of time varying much, according to the nature and strength of the solutions employed and the condition of the material under treatment. It is very generally believed that the chemicals ordinarily employed—caustic soda particularly—in "de-gumming" have the effect of breaking up the fibre in such a manner that it becomes short and "yields a weak product in commercial usage." In some instances, in which the solutions used were, through ignorance on the part of the operators, too strong, I have found this to be only too true; but, unfortunately, the breaking up also occurs to some extent in processes where neither acids nor alkalis are employed. Possibly, as the long ramie fibres are composed of small fibrils, the weakness caused by the "de-gumming" operation arises from the original fibres being broken up or separated into these smaller fibrils. I have it on the authority of Mr. Henry Ferguson, of Phoenix Mills, Brighouse, Yorkshire,—an expert possessing exceptional knowledge of ramie and vegetable fibres generally, and of their practical manipulation "from the field to the loom,"—that, whatever may be said to the contrary, the safest and most economical means of freeing the fibre from the "gum," pectic, and other bodies with least injury to its quality is the skilled use of hot alkali solutions in the first stage of operations. Those authorities who contend that the best practical results would be obtained with ramie fibre by spinning it in a condition "more nearly that in which it occurs in the plant," are reminded by an experienced spinner like Mr. Ferguson that the fibre must be first treated chemically "in order to stand the test of spinning"; in other words, the fibre in its natural condition cannot be advantageously employed for the finer textile purposes. It may be here incidentally mentioned that Mr. Ferguson has, after many years' work, succeeded in perfecting a rapid chemical means of almost

simultaneously de-barking and de-gumming the ramie ribbons without the aid of softening machinery, and so preparing the fibre as "to fit it for all the branches through which it has to be put in order to yield a strong and even yarn." This important invention is applicable to other vegetable fibres besides the one under notice.

According to Nodin and Brettoneau, the average composition of ramie stalks after de-gumming and drying may be stated as follows:—

Textile fibre	30 per cent
Wood	55 "
Bark, &c.	15 "

Dr. Collyer, by prolonged digestion in a simple soap solution, obtained 150 lbs. of pure fibre from a ton of green stalks. In Assam it has been found possible to obtain two tons of fibre per acre—from four successive crops grown in one season. The proportion of gum, pectic substances, and bark in the dried ribbons I found to vary from 20 to 30 per cent. But the proximate analyses of the ribbons I have been able to make are in some important respects imperfect, and I therefore refrain from quoting them, contenting myself with the hope that time and opportunity may enable me to hereafter deal exhaustively with that part of the subject.

Before passing on to treat of the ramie crop and the likely effect of its continuous growth and removal on the plant-food resources of the soil, I may briefly mention certain facts regarding the wild or uncultivated variety of the plant. It is met with in abundance in Japan, Java, South America, the Phillipines, and other countries, and is generally believed to yield fibre of inferior quality, but Mr. Ferguson informs me that, working on a manufacturing scale with "brown ribbons" from South America, Assam, and elsewhere, he obtained an average return of about 70 per cent of pure fibre which was in every respect equal to the product given by the cultivated plant; indeed, it could be spun with cocoon silk in the proportion of one-third of the latter to two-thirds of the fibre, yielding a fabric which even experts could not easily distinguish from pure silk, and which was found to take the same dyes as the latter. Fibre which I had myself prepared from wild ramie I found to possess practically the same strength, dye-taking power, lustre, and other qualities as the product separated by the same means from the bark of the cultivated plant.

It may be interesting to quote the following analysis of the dried stalks and leaves of wild ramie from Japan:—

	Stalks.	Leaves.
Ash	4'94	18'72
Nitrogen	0'49	1'06
The ash contained—		
Potash	32'07	4'11
Soda	10'01	0'90
Lime	20'07	34'21
Magnesia	8'27	6'51
Phosphoric acid	14'48	4'81
Sulphuric acid	3'11	1'84
Silica	3'41	42'50
Chlorine (Cl ₂ —O = 55)	2'46	1'03

The ash of a whole plant (*B. calophleba*), indigenous to Lord Howe's Island, and sent to me by the late Baron Sir Ferdinand von Mueller, F.R.S., had the following composition:—

Ash	8'87 per cent
Nitrogen	1'65 "
The ash contained—	
Potash	5'57 "
Soda	2'08 "
Lime	33'05 "
Magnesia	7'09 "
Ferric oxide	1'83 "
Phosphoric acid	5'75 "
Sulphuric acid	2'07 "
Silica	36'98 "
Chlorine (Cl ₂ —O = 55)	2'45 "

It would not, of course, be wise to infer too much from these analyses, but, if anything, they would indicate that, at all events, the wild varieties of *Boehmeria* contain an appreciably lower percentage of nitrogen and a generally similar quality of ash when compared with the cultivated plant. However, be this as it may, I quote the figures for what they may be worth, and I do so because I am unaware that any other analysis of the uncultivated plant is on record.

I have during the last five years accumulated a mass of analytical data concerning the composition of the ramie plant and its parts, but I cannot very well utilise it on this occasion, except in a general way, and that only so far as it throws light on the chemical effects likely to be produced on the soil by the continuous removal of crops from the same land.

In the following statement are arranged the analyses of the different parts of the cultivated ramie plant grown in Algeria, South America, Assam, Japan, Java, and England (Kew Gardens):—

- I. Stalks from which the bark had been stripped.
- II. Bark with fibre, gum, &c. (ribbons).
- III. Leaves.

I.
(Six Analyses).

	Minimum.	Maximum.	Average.
Total ash	3'10	3'49	3'25
Total nitrogen	0'81	0'92	0'82
The ash contained—			
Potash	36'88	38'08	37'58
Soda	9'01	16'00	10'86
Lime	16'07	17'98	17'52
Magnesia	10'63	11'20	10'67
Phosphoric acid	16'13	16'51	16'39
Sulphuric acid	2'62	3'78	3'51
Silica	1'29	2'15	1'81
Chlorine (Cl ₂ —O = 55)	1'93	2'19	2'03

II.
(Eight Analyses).

	Minimum.	Maximum.	Average.
Total ash	1'69	2'05	1'75
Total nitrogen	1'20	1'35	1'28
Ash contained—			
Potash	30'98	33'68	32'57
Soda	8'54	9'97	8'01
Lime	20'93	22'59	22'66
Magnesia	10'06	11'64	11'33
Phosphoric acid	10'88	13'04	12'57
Sulphuric acid	3'90	4'08	3'96
Chlorine	2'87	3'28	2'98
Silica	6'04	7'31	6'27

III.
(Four Analyses).

	Minimum.	Maximum.	Average.
Total ash	19'80	20'69	20'28
Total nitrogen	2'48	2'85	2'65
The ash contained—			
Potash	3'86	4'57	4'21
Soda	0'81	2'94	2'54
Lime	32'56	35'55	34'73
Magnesia	5'08	8'69	6'78
Phosphoric acid	5'09	5'85	5'27
Sulphuric acid	1'17	2'30	2'13
Silica	40'91	43'72	43'04
Chlorine	3'08	5'71	3'64

These results all refer to dried samples. In newly-cut stalks and leaves from the Royal Gardens at Kew, I found 90'86 and 90'59 per cent of water respectively.

The ramie plant thrives in a wide variety of soils, but best in rich friable loams containing humus, and preferably in localities where irrigation can be occasionally resorted

to. Under these conditions it ordinarily gives three crops a year, and in some countries—California, for example—it yields four. The presence of salt in the soil appears to be beneficial to ramie; indeed, Professor Hilgard says it is one of the very few crops which will prosper on "alkaline" land. On account of their richness in albumenoids, the leaves when green are very much liked by cattle, and for the same reason they can, according to Professor Dyer, F.R.S., be turned to account in feeding silk-worms.

Ramie is what may be termed a somewhat exhausting crop—drawing from the soil large quantities of plant food. Thus, a yield of nine tons of dried stalks and four tons of foliage would remove from an acre about 320 lbs. of nitrogen, 230 lbs. of potash, 140 lbs. of phosphoric acid, and no less than 600 lbs. of lime. An annual drain of this kind could not but ultimately tell upon the resources of even a naturally rich soil, and render it needful to resort to manuring in order to maintain fertility.

The Laboratory, 29, Fenchurch Street, E.C.

A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM, AND DIDYMIUM, AND ITS APPLICATION TO THE ANALYSIS OF MONAZITE.*

By FLOYD J. METZGER.

(Concluded from p. 230).

Effect of Salts with Acetic Radicals on the Precipitation of Thorium by Fumaric Acid.

A VERY peculiar effect is noticed when an acetate is added to a solution of the rare earths (cerium, lanthanum, didymium, &c.) which has already had added to it some fumaric acid. The results are these:—

Take a solution of cerium (lanthanum or didymium) in 40 per cent alcohol and add to it a solution of fumaric acid; nothing results. If, now, one or two drops of ammonium acetate is added to this mixture of cerium and fumaric acid, the cerium is precipitated completely. Then if to this solution containing the precipitate an excess of ammonium acetate is added, the whole re-dissolves and leaves a clear solution. Cerium (lanthanum or didymium) is not precipitated by ammonium acetate alone. Ammonium fumarate precipitates cerium (lanthanum or didymium) insoluble in excess of precipitant. Add to cerium (lanthanum or didymium) dissolved in 40 per cent alcohol, fumaric acid, and then one or two drops of acetic acid, and nothing results; but then by adding to this one or two drops of ammonium acetate, the cerium is thrown down quantitatively as before. Thorium differs from cerium, lanthanum, and didymium in that the precipitate formed by fumaric acid is only partially soluble in an excess of ammonium acetate. Sodium acetate has the same effect as ammonium acetate.

The exact reaction in the above experiments has not yet been studied, but it is quite evident that salts of acetic acid must be avoided in the separation of thorium from cerium, lanthanum, and didymium by fumaric acid.

The Effect of other Metals on the Separation.

It was very desirable to know the effect of other metals on the precipitation of thorium by fumaric acid, so all the metals available were tried. The solutions in all cases (where such solutions could be obtained) were made in 40 per cent alcohol and the fumaric acid added. The following salts were tried:—

CuSO_4 ; AgNO_3 ; AuCl_3 (acid); MgCl_2 ; CaCl_2 ; $\text{Sr}(\text{NO}_3)_2$; BaCl_2 ; ZnSO_4 ; CdCl_2 ; $\text{Hg}_2(\text{NO}_3)_2$; $\text{Hg}(\text{NO}_3)_2$;

HgCl_2 ; H_3BO_3 ; $\text{Na}_2\text{B}_4\text{O}_7$; Al_2Cl_6 ; SnCl_4 (acid); SnCl_2 (acid); $\text{Pb}(\text{NO}_3)_2$; MnCl_2 ; Na_2HPO_4 ; As_2O_3 (slightly sol.); Sb (tartar emetic); $\text{Bi}(\text{NO}_3)_3$ (slightly sol.); $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$; VOCl_2 ; Na_2WO_4 ; Fe_2Cl_6 ; FeSO_4 ; CoCl_2 ; NiCl_2 ; $\text{H}_2\text{P}_2\text{Cl}_6$.

Of the above-named salts, AgNO_3 , $\text{Hg}_2(\text{NO}_3)_2$, and $\text{Hg}(\text{NO}_3)_2$ were the only ones which gave any precipitation. The precipitation of mercurous nitrate appears quantitative as well as the precipitation of mercuric nitrate, while mercuric chloride gives no precipitate whatever. The precipitation of silver nitrate is only a partial one.

Among the rare earths obtainable were yttrium, samarium, gadolinium, erbium, and zirconium, which, dissolved in 40 per cent alcohol, gave with fumaric acid:—

Yttrium gives no precipitate cold or hot. Samarium gives no precipitate cold or hot. Gadolinium gives no precipitate cold or hot. Erbium gives a very slight precipitate in the cold, which seems to increase somewhat on heating. Only a very small fraction, however, is thrown down. Zirconium gives a quantitative precipitation on heating.

The Composition of the Precipitate formed by Thorium and Fumaric Acid.

To determine the composition of the thorium fumarate, a quantity of pure salt was prepared by precipitating the purified thorium solution with fumaric acid, washing very thoroughly with 40 per cent alcohol, and drying. The salt was first dried at 105°C . in an air-bath, and then to determine the point at which the salt was decomposed, the temperature was gradually raised, causing a gradual loss in weight until at 202° to 205°C . it became practically constant, and no indications of decomposition were evident even at 245° to 247°C . This dried salt, however, re-absorbed moisture to a considerable extent when exposed to the air.

In order to obtain concordant results, the water was first driven off at 105°C ., collected, and weighed as atmospheric moisture. For this purpose a large tin can, provided with a thermometer, was placed upon the combustion furnace, and the tube passed through in the reverse position. Air was passed through the tube and the temperature maintained at 105° for four hours; the absorption tube was weighed, the can removed, and the combustion made in a current of oxygen. The water obtained in this was calculated as water of composition. The residue left in the boat should be thoria, and was weighed as such.

A number of combustions made in the above manner gave no constant results for hydrogen, while the thorium-carbon ratio was practically 1:4, as is seen from these results:—

	ThO ₂ .	CO ₂ .	Ratio.
I... ..	0.1319	0.0883	1:4.01
II... ..	0.1606	0.1086	1:4.05

The above ratios were calculated from the thoria just after removal from the furnace. After the combustion had been completed and the boat (containing the thoria) weighed, it was placed in a platinum tube and heated with a blast-lamp for ten or fifteen minutes. White fumes were given off, and the thoria decreased in weight to the extent of several milligrams. These fumes do not condense, but if made to pass through alcohol they are partially absorbed, and from this solution a very slight precipitate can be thrown down with ammonia. The losses were:—

0.1606 gm. thoria lost on ignition	0.0039 gm.
0.1147 gm. thoria lost on ignition	0.0036 gm.
0.1403 gm. thoria lost on ignition	0.0053 gm.
0.1641 gm. thoria lost on ignition	0.0054 gm.

Being under the impression that this loss was incurred by the co-precipitation (by fumaric acid) with thorium, of some compound which on ignition with the blast yielded a volatile oxide, it was thought advisable to prepare a

* Contribution from the Havemeyer Laboratories, Columbia University. Read at the meeting of the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxiv., No. 10.

quantity of thorium fumarate from thorium which had been precipitated with fumaric acid and thoroughly ignited. This was done in the following way:—The pure thorium solution was precipitated in the usual way with fumaric acid, and ignited for a period of one and one half hours in the strongest heat that could be obtained from a blast-lamp. The thorium was again brought back into solution after many evaporations with concentrated sulphuric acid, precipitated with ammonia, filtered, re-dissolved in nitric acid, evaporated to dryness, taken up in water, and re-precipitated with fumaric acid, thoroughly washed, and dried.

Combustions were then made on this compound as before:—

	ThO ₂ .	CO ₂ .	Ratio.	Loss on ignition.
I. ..	0.1870	0.1270	1 : 4.07	0.0066
II. ..	0.2434	—	—	0.0073

The same white fumes were driven off on ignition with the blast, causing a corresponding decrease in the weight of thorium left after combustion.

To learn whether the white fumes were a carbon-containing compound or not, the platinum tube was connected to the combustion furnace, and then heated with a blast. No increase in weight was obtained in the soda-lime tube, showing the absence of carbon, but an increase, slightly greater than the loss in weight of thorium, was found in the water-absorption tube (pumice and sulphuric acid).

To find out whether the fumaric acid employed was pure and free from any non-volatile substance, several portions were burned at a gentle heat in a Bunsen flame; no residue was left. A combustion of the acid was also made, giving:—

	Calculated.	Found.
H.	3.44	3.42
C... .. .	41.38	41.302

The fumaric acid was pure, and the white fumes obtained by the ignition of the thorium fumarate are as yet unaccounted for. These white fumes, however, will be made the subject of a separate investigation. The only conclusion to be drawn from the above work is that the thorium and fumaric acid react molecule for molecule. It is not supposed that the unsaturated valencies in the fumaric acid play any part in the reaction, but rather that fumaric acid is of just the proper strength to throw out the very feebly basic thorium.

Monazite Analysis.

To test the application of the fumaric acid to the analysis of monazite sand, three samples were procured: two Brazil sands and one from North Carolina,* and to check the results obtained, two of the best known methods, the thiosulphate and ammonium oxalate separations, together with a third,—a combination of the thiosulphate and oxalate,—were employed.

A description of the methods used is as follows:—

Ammonium Oxalate Separation.—About 1 grm. of the sand, ground to an impalpable powder, was weighed out into a platinum vessel, covered over with 15 to 20 c.c. concentrated sulphuric acid, and evaporated on an asbestos board until fumes were no longer driven off. More sulphuric acid was added, and this repeated several times until the conversion of the phosphates into sulphates was complete.

This mass was then projected in very small quantities into about 700 c.c. water at 0° C. with constant agitation the temperature was not allowed to rise above 2° C.). This was allowed to stand several hours with frequent stirring, was filtered and washed.† The filtrate was then nearly neutralised with dilute ammonia (1 : 20) and 50 c.c. of a cold saturated solution of oxalic acid added (for each

grm. of ore taken), stirred well, and allowed to stand. After the heavy white precipitate had settled completely, the solution was filtered, washed, and the precipitate washed into a 400 c.c. beaker, using a cold saturated solution of ammonium oxalate for the purpose. After making the volume of ammonium oxalate equal to about 50 c.c. the beaker was placed on a water-bath, covered with a watch-glass, and digested for one and one-half hours with occasional stirring. This was then diluted to 300 c.c., and allowed to stand over night, filtered (filtrate A), and washed. The residue was again subjected to the treatment with ammonium oxalate, &c., and filtered (filtrate B).

Filtrates A and B were combined and precipitated by a large excess of ammonia, heated to boiling, filtered, and the thorium hydroxide dissolved off the filter in hot dilute nitric acid; evaporated to dryness, the residue taken up in water, and precipitated with oxalic acid. This precipitate of thorium oxalate, which still contained some impurity, was again treated with ammonium oxalate as before (one treatment), precipitated with an excess of ammonia, converted into the oxalate, ignited, and weighed as thorium dioxide.

Thiosulphate Method.—The mineral was decomposed and brought into solution as before, and precipitated with oxalic acid. The precipitate of oxalates was washed into a beaker and treated with a strong solution of caustic potash (about 25 c.c.); heated to boiling (this converts the oxalates into hydroxides, which are then quite soluble in acids), diluted, and filtered; washed thoroughly, and dissolved off the filter in hot dilute hydrochloric acid (1 : 1); evaporated to dryness to free from acid, taken up in 75 to 100 c.c. water, and 15 c.c. of a saturated solution of sodium thiosulphate added, and heated to boiling (this precipitates nearly all the thorium together with a trace of impurity and considerable sulphur); filtered (precipitate A), and the filter set aside for subsequent filtration. The filtrate was precipitated by an excess of ammonia, filtered, washed, dissolved in hydrochloric acid, evaporated to dryness, taken up in water, and re-precipitated with thiosulphate as before. This was filtered through the paper containing precipitate A. The precipitation with thiosulphate was repeated, in the successive filtrates, as long as a precipitate was obtained (usually a third precipitation extracts the thorium completely).

The combined precipitates of thorium thiosulphate were washed completely, then dried and ignited. The ignited mass was fused several times with potassium bisulphate, taken up in water and a few drops of hydrochloric acid, and precipitated with oxalic acid. These oxalates were converted into the hydroxides as before, dissolved in hydrochloric acid, evaporated to dryness, taken up in water, and re-precipitated with sodium thiosulphate; filtered, washed, dried, and ignited. This was again fused with bisulphate, dissolved in water and a few drops of hydrochloric acid, and precipitated with oxalic acid; filtered, washed, ignited, and weighed.

It was necessary to fuse the thorium several times with bisulphate to get it all into solution.

Combustion Method.—Inasmuch as the methods just described are very lengthy and involve very troublesome processes, such as the repeated digestion of a large bulk of oxalates with ammonium oxalate, or the repeated fusions necessary in the thiosulphate method, it was found very convenient to make a combination of the two. Another point, well worth mentioning, and shortening the process greatly, is the conversion of the thorium thiosulphate back into the nitrate without ignition and repeated fusions. This is very easily and quickly done by washing the precipitate of thorium thiosulphate into a beaker with water, adding 20 to 25 c.c. of a strong solution of caustic potash, and heating to boiling. The thorium is converted completely into the hydroxide, while at the same time any free sulphur is dissolved by the caustic potash. The mass then is simply brought to boiling, diluted, filtered, washed, and dissolved off the filter in dilute nitric acid.

* It was through the kindness of Professor Baskerville that we secured this sample of North Carolina sand.

† Preliminary experiments showed that no metals precipitable by hydrogen sulphide were present, so this part of the process was omitted.

As has been noticed, the same reagent (caustic potash) serves for the conversion of the oxalates into hydroxides, which are then easily converted into the nitrates.

The combination method is as follows:—

Decompose the mineral as usual, and precipitate the rare earths as oxalates; filter, and wash the oxalates into a beaker; add 20 to 25 c.c. of a strong solution of caustic potash, and heat to boiling; dilute, filter, and wash. Dissolve the hydroxides off the filter with hot dilute hydrochloric acid (1:1), and evaporate to dryness on a water-bath. Take up with water, and add 25 to 30 c.c. of a saturated solution of sodium thiosulphate; heat to boiling, filter, and wash (precipitate A), and set the filter aside for subsequent filtration. Precipitate the filtrate with an excess of ammonia, filter, wash, dissolve off the filter with hot dilute hydrochloric acid, and evaporate to dryness. Take up with water, and re-precipitate with thiosulphate as before. Filter this precipitate through the paper containing precipitate A. Wash, then wash into a beaker, and add 20 to 25 c.c. of a strong solution of caustic potash, and heat to boiling. Dilute, filter, and wash. Then dissolve off the filter in warm dilute nitric acid, and evaporate to dryness. Re-dissolve in water, and precipitate with oxalic acid; filter, wash, and rinse into a beaker, using a cold saturated solution of ammonium oxalate for the purpose (about 100 c.c.).* Digest this on a water-bath for one and one-half hours (covered with a watch-glass), dilute to 300 c.c., and allow to stand over night. (The undissolved residue of cerium, lanthanum, didymium, &c., is so slight that it need not be re-treated). Filter, and precipitate the thorium from the filtrate with a large excess of ammonia. Filter, dissolve in dilute nitric acid, evaporate to dryness, take up in water, and precipitate the thorium from this with oxalic acid. Filter, wash, ignite, and weigh.

The above method gives very satisfactory results, and yields a white oxide of thorium.

Fumaric Acid Method.—The three methods just described are very long and tedious. In many instances the solutions must be allowed to stand over night, and the precipitations repeated several times to insure a complete separation. The minimum time required to execute any one of these methods is from five to six days.

The method about to be described has the great advantage of being extremely short, requiring only about one and one-half days after the decomposition of the mineral, and gives accurate results. The method is as follows:—Decompose about 1 grm. of mineral as before, and precipitate the oxalates; wash, then rinse into a beaker, and add 20 to 25 c.c. of a strong solution of caustic potash; heat to boiling, dilute, filter, and wash. Dissolve off the filter in warm dilute nitric acid (1:1), and evaporate to dryness on a water-bath. Take up in 50 c.c. water, then add alcohol and water in such proportions as to make the solution 40 per cent alcohol (dilution = about 200 c.c.). Then add 20 to 25 c.c. of fumaric acid (0.1 grm. per 10 c.c.), and heat to boiling. Filter, while still hot, through a long-stem funnel (or by suction), wash several times with hot 40 per cent alcohol, then return precipitate and paper to the beaker, and add 25 to 30 c.c. of dilute hydrochloric acid (1:1); heat to boiling, dilute a very little (keep down the volume as much as possible), and filter off the paper. Wash the paper several times, then evaporate to dryness on a water-bath, shaking from time to time, and washing with a few drops of water to prevent the residue from clinging to the sides of the beaker. Add about 50 c.c. water (while still on the water-bath, and stir the residue loose from the bottom with a rubber-capped rod. (The carbonaceous matter from the partly decomposed fumaric acid, &c., does not interfere). Add alcohol and water to make the solution 40 per cent (dilution about 150 c.c.), then add about 10 c.c. fumaric acid, and heat to

boiling. Filter through a long-stem funnel, wash with hot 40 per cent alcohol, ignite (without previous drying) in a platinum crucible, and weigh the thorium dioxide. In this method hydrogen sulphide need not be passed through the solution before precipitation with oxalic acid, for, as has been shown, none of the metals precipitable by hydrogen sulphide interfere.

A comparison of the analyses of the three samples of sand, made by the methods described, is given in the following table. Results are given in percentages of thoria:—

	Methods.			
	Fumaric.	Oxalate.	Thiosulphate.	Combination.
Brazil (a) . .	{ 2'41	2'77	2'11	2'48
	{ 2'55	2'03	—	—
	{ 3'95	—	—	4'03
North Carolina	{ 4'02	—	—	3'76
	{ 3'92	—	—	—
	{ 2'51	—	—	2'42
Brazil (b) . .	{ 2'47	—	—	2'56

Conclusions.

1. A saturated solution of fumaric acid in 40 per cent alcohol precipitates thorium completely from neutral solutions, to which, 40 per cent of their volume of alcohol has been added, while under these conditions the only other metals that give precipitation are zirconium, erbium, silver, and mercury.

2. This precipitation serves as an accurate and rapid separation of thorium from the other earths in monazite, and by its use the thoria can be determined in about one-third the time required by the methods now in use, and with equal, if not greater, accuracy.

3. As the thorium-carbon ratio in thorium fumarate is 1:4, thorium and fumaric acid react molecule for molecule.

4. By the aid of a blast-lamp, white vapours are driven off from the thoria left in the boat after the combustion of thorium fumarate in a stream of oxygen (a fact as yet not explained).

5. Rare-earth oxalates and thorium thiosulphate are completely converted into the hydroxides by heating to boiling in a strong solution of potassium hydroxide, giving a convenient method for the conversion of those salts into the nitrates.

This investigation was carried out under the direction of Professor Edmund H. Miller, and I wish here to express my most sincere thanks to him for his kind interest and encouragement in the work, and for the valuable assistance rendered.

PROCEEDINGS OF SOCIETIES.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

Ordinary Meeting, November 4, 1902.

Mr. CHARLES BAILEY, President, in the Chair.

A PAPER on "The Action of Alkalis on Glass and on Paraffin" was read by Mr. FRANCIS JONES, M.Sc., F.C.S., F.R.S.E.

He pointed out that, while it is generally acknowledged that alkalis in course of time act on glass, there is considerable difference of opinion among chemists as to whether this action interferes with the well-known test for carbon dioxide in air, generally known as Pettenkofer's, but which was first described by Dalton in a paper read before this Society in 1802. Solutions of lime, strontia, and baryta of known strength were left in glass bottles at the ordinary temperature for several months, and the strength of each was ascertained from time to time. It was found that the lime-water lost strength more rapidly

* By this process the oxalate to be digested with ammonium oxalate is almost pure thorium oxalate and goes into solution very easily. Usually only the faintest residue of impurities remains after one digestion.

than the others, and that baryta could be kept in glass bottles for a period of twenty months without suffering any material loss in strength. Similar solutions were left in contact with finely divided silica and with powdered glass, and again it was found that lime-water acted on these bodies more rapidly than the other two. The action on glass bottles, however, is not so rapid as to prevent any three of these alkaline solutions being used for Pettenkofer's test. It has been suggested that bottles used for this test should be coated with paraffin wax, to prevent the contact of the alkaline liquid with the glass, but the author shows that lime, strontia, and baryta lose strength in contact with paraffin, the action of baryta being much more energetic than that of either lime or strontia. Some baryta solution in contact with paraffin for five months was very nearly neutral at the end of that period. Consequently, the storing of standard baryta solutions in paraffined bottles is quite inadmissible.

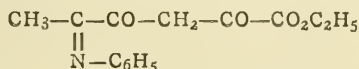
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 16, October 20, 1902.

The Formation of Liquid Drops and Tate's Law.—Ph. A. Guye and F. Louis Perrot.—The authors endeavour to explain the complex phenomena taking place during the formation of drops issuing from the extremity of cylindrical tubes with capillary bore. They also examine the successive forms each drop takes before its fall. A photographic record gives evidence quite independent of retinal illusions. They find once again that the classic relations of Tate do not correspond to the actual facts, for the rupture of the drop does not take place when it has a diameter nearly that of the tube; also that the fall of the drop preceded by the formation of a thread ought rather to be compared to the phenomena of rupture of metallic threads under a dragging force, and that consequently the rigidity of liquids ought to play a part in the formation of drops, which part still remains to be investigated.

Derivatives of Pyruvyl Pyruvic Ether. Stereoisomeric Hydrazones.—L. J. Simon.—The consecutive actions of aniline and strong sulphuric acid on ethyl pyruvate lead to the preparation of a body to which the author assigns the formula—



and which therefore may be considered as a phenylimine derivative of pyruvyl pyruvic ether. In order to prove the ketonic nature of this compound he submits it to the action of the characteristic reagents for such substances—first, to that of phenylhydrazine, and then to that of concentrated sulphuric acid.

Action of Mixed Organo-magnesium Compounds on the Ethers of the Ketonic Acids.—V. Grignard.—The author has already shown that the β -ketonic ethers generally give with organo-magnesium compounds abnormal reactions in which above all the presence of the enolic form is predominant. Such is not the case with the other ketonic ethers, which are capable of reacting normally by their two-functional grouping. But, as it may be predicted, these two groups do not present the same reaction velocity; carbonyl reacts always before carboxyl, if the method allows of the tertiary alcoholic acids being obtained or the bitertiary glycols, which happens when one molecule or three molecules of the organo-magnesium compound acts on one molecule of the ketonic ether. The author is mainly concerned with the synthesis of acid

alcohols. In his experiments, at each instant it was necessary to avoid the presence of an excess of the organo-metallic compound, so as to prevent it acting on the carboxalkyl, and to do this it was essential to allow the magnesium compounds to fall little by little into the ketonic ether. His experiments were performed on isoamyl pyruvate, ethyl phenyl glyoxylylate, ethyl levulate, and ethyl acetyl succinate. A list of results is given.

MISCELLANEOUS.

Some Crystallised Alloys of Aluminium.—O. Brunk.—*Copper and Aluminium*, Cu_4Al_9 .—Equal weights of the two metals are melted together, and very fragile, crystalline, white ingots are obtained. By decanting before complete solidification magnificent lance-like crystals can be obtained; density = 4.118. These crystals are slightly attacked by nitric acid, partially by hydrochloric acid, and completely by aqua regia. *Iron and Aluminium*, FeAl_3 .—One part of iron is melted with three parts of aluminium, and then treated with 2 per cent hydrochloric acid. Pointed crystals of an iron-grey colour are obtained; soluble in strong acids; density = 3.734. *Nickel and Aluminium*, NiAl_3 .—This occurs in crystals similar to the last, and they have the same colour as nickel; density = 3.681. *Cobalt and Aluminium*, $\text{Co}_3\text{Al}_{13}$.—Crystals of a similar appearance; density = 3.492. *Manganese and Aluminium*, Mn_2Al_7 .—Under a layer of common salt, we melt one part of manganese and six parts of aluminium, and then treat with 2 per cent hydrochloric acid. White crystals are formed having the appearance of tin. *Platinum and Aluminium*, $\text{Pt}_3\text{Al}_{10}$.—This compound requires a prolonged fusion. Rather indistinct crystals are formed of a bronze colour, decomposed by concentrated hydrochloric acid; density = 6.688.—*Berichte*, vol. xxxiv., p. 2733.

Estimation of Sulphuric Acid in Mineral Waters.—L. W. Winkler.—Sulphuric acid is precipitated by a hydrochloric solution of chromate of barium. The excess of chromate being precipitated in its turn by neutralisation, the chromic acid displaced by the sulphuric acid is determined colorimetrically, by comparison with a titrated solution of chromate of potassium. The solubility of the chromate of barium in a neutral solution not being negligible, the necessary correction is determined by the equality of the tints between a known solution of chromate of barium and the equivalent typical solution of the salt of potassium. The method of procedure is as follows:—To 150 or 200 c.c. of the water under examination, we add 5 or 10 drops of fuming hydrochloric acid, then 0.1 to 0.2 gm. of chromate of barium; boil, neutralise with soda after cooling, then filter. Take 100 c.c. of the filtrate, and, at the same time, 100 c.c. of distilled water treated with a few drops of soda; pour into this latter solution the solution of chromate of potassium until the tint is the same as that of the former. The same operation being carried out on a titrated solution of sulphate of potassium containing 1 gm. of SO_3 per litre, the value in SO_3 of the water in question is easily calculated. The possible error is from 1 to 2 m.grms. per litre, and the figures thus obtained with mineral waters agree with the results obtained by the gravimetric method.—*Zett. Anal. Chim.*, vol. xl., p. 465.

Simultaneous Estimation of Cyanides and Cyanates.—Ernst Vidor.—This method depends on the solubility of cyanate of silver in dilute nitric acid. Two portions of 10 c.c. each of the 10 per cent mixture are treated with a known excess of decinormal nitrate of silver. One portion made up to 100 c.c. is filtered, and the excess of silver titrated in an aliquot part of the filtrate. The other portion is treated first with dilute nitric acid, made up to 100 c.c., and the excess of silver determined in the same manner. The difference between these two titrations gives the amount of cyanate contained

in the sample. The author criticises the propositions put forward by Feldtmann and Buttel with regard to the same estimation. Unlike them, he did not find it necessary to work at a temperature of 0° to precipitate the cyanate of silver at the same time as the cyanide. At a temperature of 25° it is only after the lapse of several hours that the decomposition of the cyanate into ammonia and bicarbonate of potassium is noticed, and not the transposition, $\text{OCNK} + 2\text{H}_2\text{O} = \text{CO}_3\text{KH} + \text{NH}_3$.—*Zeit. Anal. Chim.*, vol. xi., p. 462.

NOTES AND QUERIES.

*. * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Pure Cyanide.—We are in the market for large quantities of chemically pure cyanide, but are not informed as to who the manufacturers are in England and Scotland. We would be under obligations if you would furnish us with the names of said manufacturers.—H. P. D.

Action of Red Light.—As a constant reader of your valuable paper, I shall esteem it a favour if any of your scientific correspondents can inform me what is the action of the red rays of light on the hair, and what authority is there for supposing that they have a beneficial effect and promote the growth?—P. H. BAILY.

MEETINGS FOR THE WEEK.

WEDNESDAY, 19th.—Chemical, 5.30. "The Dynamic Isomerism of Thiourea and Ammonium Thiocyanate," by J. E. Reynolds and E. A. Werner. "Isomeric partially Racemic Salts containing Quinquevalent Nitrogen—Part VIII, Re-solution of the Hydrindamine Bromocamphor Sulphonates," and "Isomeric Compounds of the Type $\text{NR}_1\text{R}_2\text{H}_2$," by F. S. Kipping. "The Synthesis of $\alpha\alpha$ -Dimethylglutaric Acid, of β -Hydroxy- $\alpha\alpha$ -Dimethylglutaric Acid, and of the *cis*- and *trans*-modifications of $\alpha\alpha$ -Dimethylglutaconic Acid," by W. H. Perkin, jun., and Miss E. Smith. "A Reaction of some Phenolic Colouring-matters" (Part II.), by A. G. Perkin and C. R. Wilson. "The Vapour-pressures and Boiling-points of Mixed Liquids" (Part II.), by S. Young and Miss E. C. Fortey. "The Vapour-pressures and Boiling-points of Mixed Liquids" (Part III.), and "Note on Mixtures of Constant Boiling-point," by S. Young. "Note on the Condensation-points of the Thorium and Radium Emanations," by E. Rutherford and F. Soddy. The Oxime of Meosamide and some Allied Compounds—Part II., Di-substituted Derivatives," by Miss M. A. Whiteley.

Society of Arts, 8. Opening Meeting of the 149th Session. Inaugural Address by Sir William Henry Preece, K.C.B., F.R.S., Chairman of the Council.

Microscopical, 8. "An Electrical Method of taking Microscope Measurements," by Dr. Philip E. Shaw. There will also be Demonstrations on "The Microscope in Fossil Botany," by Dr. Dukinfield H. Scott, F.R.S., and on "An Apparatus for obtaining Monochromatic Light with the Mixed Jet," by Dr. Edmund J. Spilla.

In the Matter of the COMPANIES' ACTS, 1862 to 1900,

and
In the Matter of the MINERALS REDUCTION, LIMITED.

THE CREDITORS of the above-named Company are required on or before the 10th day of December next to send in their names and addresses, and the particulars of their Debts or Claims, and the names of their Solicitors (if any), to the undersigned CHARLES WHINFIELD ASTON KEY, of 2, Metal Exchange Buildings, Leadenhall Avenue, London, E.C., the Liquidator of the said Company, and if so required in writing from the said Liquidator are by their Solicitors to come in and prove their Debts or Claims at such time and place as shall be specified in such notice, or in default thereof they will be excluded from the benefit of any distribution made before such Debts are proved.

C. W. ASTON KEY,
Liquidator.
2, Metal Exchange Buildings,
Leadenhall Avenue, London, E.C.,
November 7th, 1902.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

(Founded 1877, Incorporated by Royal Charter 1885).

NOTICE IS HEREBY GIVEN, that the NEXT EXAMINATIONS of the INSTITUTE OF CHEMISTRY, for persons desirous of qualifying themselves to be Public and Technical Analysts, will be held at 30, Bloomsbury Square, London, W.C., in JANUARY, 1903.

The Examinations are open only to Candidates who have complied with the Regulations.*

The Intermediate Examination will occupy at least four days, commencing on TUESDAY, JANUARY 6th.

Examinations in the following Branches of the Final Examination for the Associateship (A.I.C.) will extend over at least four days, and may commence on either January 6th or 13th:—(a) Mineral Chemistry; (b) Metallurgical Chemistry; (c) Physical Chemistry; (d) Organic Chemistry; and (e) The Analysis of Food and Drugs, and of Water, including an Examination in Therapeutics, Pharmacology, and Microscopy.

(The Final Examination in Branch (f) Biological Chemistry is held in October each year).

Applications for admission to the January Examinations should be forwarded to the Registrar not later than TUESDAY, DECEMBER 2nd, 1902, on which day the List of Candidates will be closed.

By Order of the Council,

RICHARD B. PILCHER,

Registrar and Secretary.

30, Bloomsbury Square, London, W.C., October, 1902.

* "The Regulations for the Admission of Students, Associates, and Fellows of the Institute of Chemistry" may be obtained from Messrs. Blundell, Taylor, and Co., 173, Upper Thames Street, London, E.C. price One Shilling.

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TO MANUFACTURING CHEMISTS and OTHERS.

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Tenders, which must be upon the Official printed forms, and comply with the instructions contained therein, or be rejected, are to be delivered at the County Hall, in a sealed cover, addressed to the Clerk of the London County Council, not later than 10 o'clock a.m. on THURSDAY, NOVEMBER 27th, 1902.

The Council does not bind itself to accept the lowest or any tender, and it will not accept the tender of any person or firm who shall on any previous occasion have withdrawn a tender after the same has been opened, unless the reasons for the withdrawal were satisfactory to the Council.

Spring Gardens, S.W.,
November 12, 1902.

G. L. GOMME,
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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2243.

SOME OBSERVATIONS ON THE FLUORESCENCE AND PHOSPHORESCENCE OF DIAMONDS, AND THEIR INFLUENCE ON THE PHOTOGRAPHIC PLATE.

By OTTO ROSENHEIM, Ph.D., F.C.S.

It has been observed by W. Marckwald (*Chem. Zeit.*, xxvi., 895), that the rays emitted by radioactive polonium possess the property of inducing fluorescence in diamonds. The present writer has examined a large number of diamonds of different origin (Cape, Brazil, British Guiana, India), which all exhibited this phenomenon. The intensity of the fluorescence apparently varied with the size and quality of the diamonds, but they could all be distinguished from other precious stones, such as ruby, emerald, zircon, topaz, opal, &c., by their emission of light under the influence of polonium in an absolutely dark room.* The so-called black diamonds or carbonados were not affected by polonium.

The rays emitted by the diamond under the influence of polonium affect not only the retina, but also the photographic plate. If in the absence of actinic light a diamond and a polonium rod† placed closely together, are brought into contact with a photographic plate, development after an exposure of two minutes' duration demonstrates the reduction of the bromide of silver not only along the polonium rod, but also underneath the diamond, the image produced in this case being much more striking and sharply defined. A similar effect is observed if the distance between the diamond and rod be increased to 10 m.m. or more.

This actinic activity of the diamond, like its visible fluorescence, is entirely dependent on the presence of the polonium, not persisting after the removal of the latter. Even after long exposure to polonium rays no induced radioactivity could be detected.

Although the rays emitted by polonium and those emitted by the diamond under its influence are qualitatively alike in their effect on the photographic plate, they differ in their absorbability by various substances. As is well known, the former are easily absorbed by tissue paper, celluloid, gutta-percha tissue, and glass, and exert no influence on the plate through these. On the other hand, the rays emitted by the diamond, under the influence of polonium, easily penetrate thin films of these substances or glass plates a few millimetres thick. This may be demonstrated by interposing between the sensitive plate and the diamond and polonium rod a sheet of paper, of gutta-percha tissue, or of celluloid. On development an impression of the diamond only is obtained. The same difference of effect is observed if the diamond and polonium rod are placed in contact with the "back" of the photographic glass plate or celluloid film, the polonium rays being absorbed completely by the glass or celluloid.

The observations described seemed to make it of interest to examine the effect on the photographic plate of phosphorescent diamonds. It has been known since R. Boyle first described this phenomenon in 1663 that certain diamonds, after exposure to strong sunlight, possess the power of sending out phosphorescent light. Quite recently the late J. H. Gladstone (*Brit. Assoc.*

Report, 1902; *CHEM. NEWS*, lxxxvi., 176), added another to the many instances of this phenomenon already known. The present writer has examined a great number of diamonds with regard to the possession of this property, making use, however, in the absence of strong sunlight of the actinic light emitted by burning magnesium ribbon. Of the diamonds thus examined only three were phosphorescent. With these an exposure of a few seconds to magnesium light was sufficient to produce phosphorescence as intense, judged by the eye, as the fluorescence produced by polonium. In spite of this the phosphorescence of none of these diamonds, produced by even a long exposure to the light, had the slightest effect on the photographic plate, even after a contact with the latter extending over 24 hours. It is interesting to note that of these three diamonds two were known with certainty to be of Brazilian origin, whilst the third was described as such.

The experiments described have shown:—

1. That all the diamonds examined fluoresce and affect the photographic plate under the influence of polonium.
2. That the rays emitted by the diamonds under these conditions differ from the polonium rays by their power of penetrating various media.
3. That certain diamonds phosphoresce after exposure to magnesium light, but their rays do not affect the photographic plate.

King's College, London,
November, 1902.

THE ULTRA-VIOLET SPARK-SPECTRA OF THE ELEMENTS.

By Prof. FRANZ EXNER and Dr. E. HASCHEK.

Radium.

THE spark spectrum of radium has been investigated by Demarcay (*Comptes Rendus*, 1899, cxxix.; 1900, cxxx.), Runge (*Ann. der. Phys.*, 1900, Bd. ii.), and Berndt (*Phys. Zeit.*, 1900-1901, Bd. ii.). Considering the difficulty of obtaining the material, and its want of uniformity according to the method of preparation employed, it is not surprising that the results of the several observers, as regards the identification of the lines, do not agree in many cases. The material which we had at our disposal we obtained as chloride from the Société des Produits Chimiques, in Paris, with an activity of 240. The number of the lines which we must in all probability ascribe to radium is seventeen.

λ	i.	
2512.46	1 +	Very faint in Ba.
2736.20	1 + br.	—
2813.60	1	Very faint in Ba.
16.25	2 + br.	—
31.98	1	—
77.10	1 +	Very faint in Ba.
2908.0	1 + br.	—
76.17	1 +	—
3079.97	2	Faint in Ba.
3126.53	1	Very faint in Ba.
3541.77	1 +	Very faint in Ba.
3649.33	2 +	Faint in Ba.
3814.62	3	—
61.77	3 + *	Faint in Ba.
3993.25	3 + †	—
4053.81	1 +	Very faint in Ba.
4682.41	1	—
4781.4	1 + br.	—

* This line does not belong to radium.

† This line is very close to a strong barium line.

* It hardly needs special mention that the phenomena of fluorescence and phosphorescence described can only be observed if the eyes have been "adapted" for some time to complete darkness.

† The commercial polonium-bismuth rod, prepared according to Marckwald, was used for these experiments.

The lines which we mark as occurring also in Ba were observed in a very strongly exposed spectrum of barium nitrate. Considering the relative intensity of the strong

barium lines in the radium preparation and in barium nitrate, it is difficult to believe that these lines belong to barium. We have therefore provisionally included them in the table of radium lines. As Runge remarks, some of the lines which Demarcay ascribes to radium certainly belong to barium. However, the lines 4627·4 and 4699·8, which are both missing in our radium spectrum, differ so much in wave-length from the neighbouring barium lines that they can hardly be identified with these. The line 4641·9 belongs to oxygen. Demarcay's five lines between 4340 and 4533 were invisible to us, as also to Runge. They appear, at least in part, to belong to Ti and Ca. Of the three lines which Runge specifies for radium, we could not find the one 4826·14, which Demarcay also has observed; Berndt, too, does not mention this. On the other hand, this observer gives a line at 2708·6, which none of the other observers have seen. Only the two lines 3814 and 4682 are common to all measurements; the latter has also been observed by Miethe (*Phys. Zeit.*, Bd. 2, Feb., 1901), when investigating radium with a new spark apparatus. A second line, $\lambda = 4348$, described by him as very strong, is not mentioned by any other observer.

Polonium.

There is still more uncertainty about the spectrum of polonium than about that of radium. Demarcay (communicated by P. Curie, *Comptes Rendus*, 1898, cxxvii.) and Runge (*loc. cit.*) could find no lines. Berndt (*loc. cit.*) found fifteen, but it is very doubtful whether some of them belong to polonium. We have examined two different preparations: an older preparation by M. Curie (bismuth nitrate), with an activity of 5000; and a polonium-bismuth metal of activity 300, as supplied by the Société Centrale des Produits Chimiques. In the first we were able to discover a series of faint lines which we could not identify with any known lines. We quote them here for the sake of completeness, without wishing to affirm that they belong to polonium.

Bismuth-polonium Nitrate.

λ	i
3289·49	2 Yb?
3944·90	2 + Ho?
4167·81	2

In the second preparation we found only Fe, Bi, As. We have only given the more strongly marked lines of the first preparation. They cannot be definitely ascribed to polonium; they do not in the least agree with those which Berndt has found. Of these last, the greater number certainly belong to impurities, which, as far as identification is possible, we denote in the following table of Berndt's lines by the annexed symbols:—

λ	λ	λ
2327·3 Fe	3168·2 Ti	3462·0 Ti
2661·9 Sn? Pb?	3191·2 Ti	3467·1 Cd
2977·0 Ru	3349·2 Ti	3821·9 Rh?
3152·2 Ti	3361·5 Ti	4007·7 Ti
3162·9 Ti	3342·0 Mn?*	4596·3 O

* The wave-length appears to be wrongly placed by a printer's error.

The lines given here do not agree with ours, so that we must say that up to the present no polonium lines have been established with certainty.—*Aus den Sitzungsberichten der Kaiserl. Akademie der Wissenschaften in Wien.*

The Concise Chemical Analysis Chart.—We have received a copy of this Chart from the publishers, Messrs. Jarrold and Sons, London, and can recommend it for the laboratory use of students. The Chart contains not only instructions for chemical analysis by the ordinary group method, but also a number of confirmatory tests by the dry way, in the flame, on charcoal, &c. It is arranged in a convenient form, and is more suitable for bench-work than a text-book as generally used.

CONTRIBUTIONS TO OUR KNOWLEDGE OF YTTERBIUM.*

By ASTRID CLEVE.

I. INTRODUCTION.

Historical.

In the year 1843 Mosander discovered a new rare earth, the pink-coloured terbium earth (the erbium earth of Berlin and subsequent investigators); this new earth was afterwards subjected to further examination by Bahr and Bunsen, as well as by Höglund.

Thirty-five years later, however, Marignac (*Arch. des Sciences Phys. et Nat.*, November 18, 1878) succeeded in proving that the erbium earth was not a single substance, but that, by partial decomposition of the molten nitrate, it might be resolved into two components—a pink-coloured earth for which the old name was retained, and a colourless earth which he called ytterbium.

Owing to lack of material, Marignac could not continue the investigation of this newly-discovered colourless earth; but its further examination was carried on without delay, since L. F. Nilson (*Öfv. K. Vet. Ak. Förh. Stockholm*, 1879, No. 3) in the next year (1879) was able to issue a report on his experiments on the isolation of ytterbium. This author finally obtained an earth which in solution was completely free from all absorption-bands; its atomic weight remained constant at 132 (R^{10} , i.e., at 174, calculating from the formula of the sesquioxide); this value was slightly higher than the number obtained by Marignac—130·8 (and 172·2 respectively).

In the same investigation Nilson was led to the discovery of scandium. After continued fractionating, the atomic weight of one portion of the material was found to be considerably lower. All these fractions were taken and purified. Further examination showed that they owed their diminished atomic weight to the admixture of a new substance—scandium.

In the following year Nilson published further details concerning scandium (*Öfv. K. Vet. Ak. Förh. Stockholm*, 1881, No. 6, S. 16). He had by that time succeeded in obtaining 20 grms. of the rare earth. After careful purification and separation of the scandium, the atomic weight was fixed at 173·01 ($O = 16$); this number was not altered by further fractionating. The fact that Nilson had previously obtained a higher number, 174, is to be ascribed to the presence of traces of platinum, derived from the vessels in which the experiments were performed.

Besides the oxide, Nilson prepared the hydrate, nitrate, sulphate, acid selenite, and oxalate; the three last being also analysed. If we add that Thalén a short time afterwards described the spark-spectrum of ytterbium, we have stated all that is at present known of the metal. We may summarise our knowledge as follows:—Ytterbium is probably an elementary substance with atomic weight 173. It possesses at least one salt characteristic of trivalent metals, namely, the acid selenite. The salts have no absorption spectrum if the acid ion is colourless.

In consideration of the fact that up to the present very few reports on the characteristic properties of the metal have been published, I was induced to carry on further investigations, particularly as regards its compounds, which for the most part have not yet been described. This seemed specially desirable, since a great deal of work has recently been done on the elements most closely allied to it, e.g., gadolinium and praseodymium.

I was all the more impelled to carry on this research because fairly considerable quantities of the earth in question were to be obtained from the University Chemical Laboratory at Upsala, and this material was most kindly placed at my disposal. I take this opportunity of expressing my thanks to the Directors of the Institute, my father Professor P. T. Cleve, and Professor O. Pettersson, who

* From the *Zeitschrift für Anorganische Chemie*, xxxii.

have rendered me assistance by giving me both material and valuable advice. The work was performed in the Chemical Institute of the Stockholm High School.

II. PREPARATION OF PURE MATERIAL. THE ELEMENTARY NATURE OF YTTERBIUM. ATOMIC WEIGHT AND VALENCY.

The earth was prepared from a mixture, amounting in weight to several kilograms, of ytterbium earths derived from many different minerals. Cerium oxides were previously removed by treatment with potassium sulphate, and the recovery of pure ytterbium then fell into two sections.

Firstly, the greater quantity of ytterbium was separated according to Marignac's well-known method. Nilson had already shown that this method was preferable to Bunsen's in the case in question. Crude ytterbium can be extracted from the remaining mixture comparatively quickly if the heating of the nitrate is stopped when the consistency of a fairly mobile fluid is reached, so long as yttrium and erbium are present in considerable quantity, but the heating must be increased in proportion as the mixture is richer in ytterbium.

As a rule each greater fraction was subjected to two successive partial decompositions, and those portions were purified which showed sufficient agreement when examined spectroscopically.

In other cases, especially for the separation of erbium and holmium, the method of partial decomposition of the nitrate is long and tedious, but it is useful if it is required to separate ytterbium from greater quantities of yttrium, holmium, and erbium in this order. After the strongly marked absorption-bands caused by the erbium had disappeared in the green region, the fused nitrate still showed for some time a violet colouration due to thulium. There still remained the lengthy task of completely purifying the ytterbium earth which had been freed from erbium; for only by repeated fractionation could the ytterbium be freed from thulium without excessive loss of material. Nilson also mentions the difficulty of getting rid of all the thulium.

In this way I obtained about 150 grms. of an earth the concentrated solutions of which were colourless. It was, of course, possible that scandium was still present. The whole quantity was therefore split up into new fractions, the atomic weights of which were determined in the ordinary way by converting the oxide into sulphate.

I found the following values for the first—least basic—fractions, in which the scandium must be present in greatest quantity.

(NOTE.—In this, as in all subsequent calculations, the atomic weights established by the Commission on Atomic Weights are employed).

I	..	..	..	..	..	173.3
2	..	..	..	..	..	172.8
3	..	..	..	..	..	172.1
4	..	..	..	..	..	172.9
5	..	..	..	..	..	172.3

Hence it follows immediately that scandium was not present to a perceptible extent.

The original material was now split up into five parts, and their atomic weights were ascertained:—

		Oxide. Grm.	Sulphate. Grm.	Atomic weight.
I.	..	0.3919	0.6319	172.15
II.	..	0.4793	0.7728	172.15
III.	..	0.3693	0.5963	171.4
IV.	..	0.6121	0.9867	172.23
V.	..	0.6842	1.1027	172.34

Since the atomic weights agreed so closely that the earth might be regarded as tolerably homogeneous, it was subjected to a last purification, in accordance with Nilson's directions (*Ofv. K. Vet. Ak. Förh. Stockholm*, 1880, No. 6, p. 6), in order that any foreign matter which

had been introduced during the process of separation might be removed. In the first place, a small quantity of the platinum of the dishes always goes into solution. In order to ascertain the influence of this platinum on the atomic weight, all the platinum from Fraction III. above was removed by means of sulphuretted hydrogen, and the neutral solution after filtration was precipitated with oxalic acid (III a).

Ammonia still gave a small precipitate in the filtrate III. b. The atomic weights of the two fractions were:—

	Oxide. Grm.	Sulphate. Grm.	At. weight.	Colour of oxide.
III. a.	0.4204	0.6800	170.86	Faint brown.
III. b.	0.5739	0.9271	171.14	Yellowish brown.

Thus, before purification, the presence of platinum caused the value found to be too high by unity, or at the least by one-third.

When all the material had been similarly treated, the last traces of foreign earths were removed by decompositions of the nitrate. The highest atomic weights thus obtained were those of the three fractions—

Oxide. Grm.	Sulphate. Grms.	Atomic weight.
0.7791	1.2535	173.22
0.5190	0.8353	173.05
0.4905	0.7894	173.07
Mean		173.11

Further decomposition of these fractions did not lead to higher values.

The number 173.01 fixed by Nilson corresponds to 173.16 after correction for the atomic weights employed throughout these calculations, and thus agrees with my mean value given above, within the limits of experimental errors. Hence I saw no reason for further investigating the atomic weight or elementary character of ytterbium, but contented myself with confirming Nilson's conclusions on these points. The atomic weight 173.11 may be taken as accurate to the first decimal, and will be used as the basis of all calculations.

Obviously, it is not impossible that ytterbium might be decomposed by hitherto unknown or untried methods. However, I have not been able to discover any indication that this is the case, and at present no reason for doubting the elementary nature of ytterbium appears to exist.

Only one oxidation product, the sesqui-oxide, is known. An attempt to obtain lower oxides was unsuccessful. The oxalate was moderately heated in an uncovered crucible until the weight became constant, the residue weighed, and then again ignited in the open crucible before the blowpipe, without any alteration in weight taking place. The oxide thus obtained was identical with the substance prepared by igniting the nitrate.

Before I pass to the description of the ytterbium compounds, I must mention that for the preparation of some of these an earth was used which had an atomic weight somewhat lower than the theoretical.

It was not possible, without sacrificing too much of the material, always to reach the right value. Hence in some analyses the percentage of ytterbium was found to be a little too low. In other cases, on precipitation with oxalic acid, a similar result was obtained, owing to the fact that the oxalate is slightly soluble. As will be proved later, the salt is among the most soluble of the oxalates of the rare earths. Precipitation with ammonia is therefore much to be preferred for analytical purposes.

All determinations of specific gravity were made according to O. Pettersson's directions (*Ber.*, ix., 1559), by weighing in benzene from which the air has been expelled by boiling under diminished pressure. The values given are referred to the temperature of the room. The specific gravity of the benzene was determined independently each time.

(To be continued).

ON RADIUM AND RADIO-ACTIVE SUBSTANCES.

By F. GIESEL.

In a recent communication to No. 24 of the third annual volume of the *Physikalische Zeitschrift* I have shown that radium has a characteristic pure carmine-red flame colouration and a bright flame spectrum. This latter differs conspicuously from Demarcay's spark spectrum, in that two broad intense lines appear in the orange-red, while the spark-spectrum only exhibits two very faint lines in this region; these lines have not been further investigated. Professor Runge is going to be kind enough to determine the spark-spectrum of radium.

Furthermore, using the pure radium bromide, I had been able to confirm my earlier observation of the constant liberation of bromine (F. Giesel, *V. d. Phys. Ges.*, II. Sitzung, vom January 5, 1900) from the salt containing barium (in addition to the ozonisation of the air). I have now also proved the effect of this liberation of bromine, namely, the formation of radium hydroxide (with alkaline reaction) and radium carbonate formed from it (by the action of the carbon dioxide of the air). The proof that the reaction of the radium bromide becomes alkaline is rendered more difficult because the solution bleaches litmus in consequence of the formation of a salt of hypobromous acid. As this gradual splitting up of the radium bromide proceeds a gas is disengaged. The crystals occlude a part of this gas, and give it up with decrepitation on solution in water. Hence, when solution begins they become milky. Exactly the same processes occur not only in the solid salt but also in the solution. This becomes yellow owing to the presence of free bromine which remains dissolved, and a colourless gas is constantly disengaged. This gas may be collected in the pure state by filling pipettes with the solution of the radium salt and allowing the gas as it escapes to displace the liquid. After Curie's researches on induced activity, it is not surprising to find that this gas is exceedingly active, causes phosphorescence, and in a very short time colours the glass pipettes.

It was most probable that the gas was hydrogen, but a mixture with one-third volume of oxygen in a pipette did not explode when a flame was applied. Should the spectral analysis of the gas, which is now in course of progression, show that the gas does not originate from the decomposition of the water, but that it is a new gas, it must be derived from the radium, and it is to be assumed that it stands in a causative relation to the induction effect of the radium. Thus an insight would be given into the internal processes of the radium atom.

The preparation of pure radium from the raw material is carried out by the method I employed three years ago (*Wied. Ann.*, 1899, lxi., 92; cf. also Ahrens, *Sammlung Chem. und Chem. Tech. Vortr.*, Bd. vii., S. 7 and 8). The raw material consists principally of barium, strontium, and calcium, and only contains very small quantities of radium (in the most favourable case only 0.3 per thousand). After converting into the bromides one crystallisation is sufficient to remove strontium and calcium. After about eight more crystallisations of the mixture of barium and radium bromide from water, the separation of the more easily soluble barium bromide is generally complete. The colouration of the Bunsen flame conveniently indicates the progress of the purification. Fractional precipitation by ammonium carbonate may also be employed for the same purpose. Radium carbonate is precipitated last.

Of other salts of radium, except the sulphate, the only coloured salt which has hitherto been prepared on account of its optical properties is the double cyanide of platinum. It scarcely differs from the salt containing barium which has previously been obtained (*Wied. Ann.*, 1899, lxi., 69; *Verh. d. d. Phys. Ges.*, II. Sitzg., v. Jan. 5, 1900), but even in the liquid becomes strongly dichroic in a few minutes (brown-red to black in crossed crystals).

The pure anhydrous radium bromide exhibits a splendid bluish phosphorescence at first, and has a continuous

spectrum. The phosphorescence decreases after one day in consequence of the appearance of a colouration; but it may be temporarily revived (decolouration produced by heating), but afterwards disappears more and more. Hence, for the demonstration of the strong phosphorescence of the bromide, a preparation containing barium is to be preferred. The Becquerel radiation of the pure radium salts is very considerable, and it is only necessary to mention that previously fused alkali haloids are coloured by them in a few minutes.

With regard to Marckwald's work on polonium (*Berichte*, 1902, xxxv., 2285), I should like to point out that the Curies call special attention to the fact that their polonium sends out chiefly easily absorbed rays, which are partly intercepted even by the thinnest aluminum foil. Marckwald has not investigated the question whether this radiation, which has been thoroughly studied by the Curies, behaves differently from that of his preparation. The polonium prepared by me—besides the easily absorbed rays which are also present (*Wied. Ann.*, 1899, lxi., 93)—at first gives rise to such powerfully penetrating rays, that I could discover in them the magnetic power of deflection of the Becquerel rays (*Wied. Ann.*, 1899, lxi., 834). The polonium gradually loses this radiation, which is rendered perceptible by the ordinary screen of barium-platinum cyanide, but it retains a residual effect, to which attention has already been called (*Berichte*, 1901, xxxiv., 3775). Thus, as regards its initial effect, my polonium has nothing to do with Marckwald's body, and hence cannot be considered with it. According to this, Marckwald's observations at present do not contradict earlier information on this point. Also, it seems to me that the assumption that the chief constituent of my polonium is bismuth rendered inactive by induction is not weakened. As before, I can obtain polonium with the properties in question out of a material which has for a long time settled in layers, and, for preference, from the active barium and lead precipitates. The dissipating induced activity is again restored, by continued induction, to bismuth which is embedded in active material.

The residual effect which has been mentioned can be derived from Marckwald's body. This, in any case, may be separated from my polonium, even if it has become almost inactive, in even larger quantity than from the rest of the bismuth often contained in considerable amount in the uranium ores. For the initial activity (induced) of my polonium this body cannot be made responsible, because this activity could not disappear in its presence.

The properties mentioned by Marckwald as characteristic of his body I can confirm, and add that the radiation—as in the case of radium—colours paper yellow in the course of several weeks. Only indications of the phosphorescence of the barium-platinum cyanide screen are to be observed on applying the preparation on the side of the stratum. On the other hand, a screen of Sidot's hexagonal blende (zinc sulphide), prepared with gelatin, reacts in such a way that it is affected as by radium salts, and afterwards emits light.* Even at some centimetres' distance the phosphorescence is easily visible; at a greater distance probably the layer of air acts as an absorbent.

For such easily absorbed rays the screen of zinc sulphide is a valuable means of observation and demonstration. In this way, in some preparations obtained from radium impurities which only possessed relatively small rectilinear radiation, I have been able to demonstrate Rutherford's emanation in a most convincing manner.

If a filter with some centigrms. of the substance is laid on the screen, the emanation spreads over a larger extent of the screen and produces a phosphorescence which is driven to and fro by the lightest current of air. By blowing, the direction can be altered at will. If the preparation is placed in a tube, by blowing with the mouth a current of air can be obtained which will act strongly on

* I notice, in addition, that Marckwald (*Phys. Zeit.*, No. 16, IV. Jahrg.) uses zinc oxide as a phosphorescent substance; it is considerably less sensitive.

the screen. The phenomenon cannot be observed with a screen of barium-platinum cyanide or a screen with Balmann's luminous paint. The emanation is not affected by magnetic forces; but, on the other hand, it is affected by electric forces. If the screen is given a negative charge by an influence machine, on bringing the substance wrapped in filter-paper close to it, it becomes luminous, and not uniformly, but the light is concentrated in a peculiar manner into points or rings (screen effect); the luminosity ceases when the preparation is removed, or when the screen is discharged or given a positive charge.

The substance giving rise to the emanation will now be examined. It appears to possess a peculiar chemical nature, as no other of the known strongly active substances or thorium earths reveals an emanation in this manner. The body is found in the ammonia precipitate after separation of the rare earths from pitchblende with oxalic acid. Possibly it is in some way connected with Rutherford's hypothetical body "ThX." The emanation does not appear to be a gas; at any rate, no disengagement of gas from the substance was observed under water.

I obtain the earths which belong essentially to the cerium group (*Berichte*, 1900, xxxiii., 3570; 1901, xxxiv., 3776) from other material of constant activity, and it is possible to purify by fractional crystallisation of the oxalates from dilute nitric acid, so that there seems to be some prospect of being able to investigate Debierne's actinium. But thorium is only present to a very small extent, and methods aiming at the separation of it no longer, as before, lead to an increased—but, on the contrary, to a diminished—activity.

Unfortunately, from the radium mother-liquor I can no longer obtain my strongly and constantly active substance (*Berichte*, 1902, xxxv., 102), which adheres to the lead, or I can only get traces of it; on the other hand, the emanation body is present here also.—*Berichte*, 1902, xxxv., 3608.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1902.

By SIR WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To CHARLES PERRIN, Esq., M.Inst.C.E.,
Water Examiner, Metropolis Water Act, 1871.

London, November 10th, 1902.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 208 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Oct. 1st to Oct. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in previous reports.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 208 samples examined by us chemically during the month, all were found to be clear, bright, and well filtered.

There is no indication yet of any break-up of the prolonged drought. The rainfall at Oxford during October was 1.55 inches; the average fall for the month is 2.76 inches, leaving a deficit of 1.21 inches; this, added to the

previous one of 6.63 inches, gives a total deficit of 7.84 inches, or 37.6 per cent on the thirty-five years' average.

Our bacteriological examinations of 536 samples have given the results recorded in the following table; besides these we have examined 38 other samples, from special standpipes, wells, &c., making a total of 574 samples in all:—

	Microbes per c.c.
New River, unfiltered (mean of 26 samples) ..	314
New River, filtered (mean of 127 samples) ..	11
Thames, unfiltered (mean of 26 samples) ..	8243
Thames-derived water, from the clear-water wells of eight Thames-derived supplies (mean of 295 samples) ..	20
Ditto ditto highest	265
Ditto ditto lowest	0
River Lea, unfiltered (mean of 26 samples) ..	243
River Lea, from the East London Company's clear-water wells (mean of 36 samples) ..	17

Of the 458 daily samples taken from the filter-wells of the Metropolitan Water Companies, and examined bacteriologically by us, twenty-seven samples, or 5.8 per cent, were sterile. Four samples contained more than 150 microbes, while twelve samples, or 2.6 per cent, contained more than 100 microbes per c.c. The mean number of microbes in the twelve excess samples was 145, against a corresponding mean of 128 in eighteen samples during September.

Considering the time of year, these figures show that the condition of the London waters is highly satisfactory from a bacteriological point of view; and the same remark also applies to its chemical characteristics.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES,
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions*:—

127. "On the Solvent Properties of Mixed Liquids in Relation to the Chemical Characters and Solvent Properties of their Components." By H. M. DAWSON.

The solvent power of mixtures of liquids in its relation to that of the components has been investigated under conditions such that complicating secondary effects of electrolytic dissociation, high concentration of the solutions, and interaction of the component liquids are avoided.

Measurements of the solubility of iodine were obtained by determining the ratio of distribution between water as standard substance on the one hand, and mixtures of organic solvents on the other. A method of determining this partition ratio is described in which an aqueous solution of potassium iodide is employed instead of pure water. If the iodine concentration in the aqueous solution remains the same in all experiments, the conditions of experimentation correspond almost exactly with the determination of the solubility of a gas in different liquids, the pressure of the gas being kept constant. The organic solvents chosen were such as would not be expected to have any action on each other, or on the dissolved iodine. In these circumstances, it is found that in the majority of cases the solvent power of the mixture is less than the sum of the solvent powers of the components; sometimes, however, it is equal to, or greater than, the sum of the solvent powers of the components. No case of a maximum or minimum solvent power, such as that observed with

alcohol-water mixtures in regard to hydrogen, oxygen, carbon monoxide, and carbon dioxide has been found.

128. "Notes on Luteolin and Apigenin." By A. G. PERKIN.

Kiliani and Mayer (*Ber.*, 1901, xxxiv., 3577) have recently asserted that the author's tetrabenzoyl-luteolin (*Trans.*, 1896, lxi., 209) is in reality a tribenzoyl derivative. A re-examination of the original preparation shows that the statement of Kiliani and Mayer is incorrect, and that the substance is without doubt tetrabenzoyl-luteolin. Further experiments with reference to the tinctorial properties of apigenin and chrysin confirm the previous results of the author (*Trans.*, 1897, lxxii., 806).

129. "Note on a Simple Form of Landsberger's Apparatus." By E. B. LUDLAM.

A description is given of an apparatus which has proved most satisfactory to work with. The tube in which the rise of temperature is measured is graduated and placed in the neck of the flask containing the boiling solvent, the vapour of which enters it from below by means of a simple valve which serves the double purpose of regulating and breaking up the stream of vapour, and also of preventing the solution from running back into an intermediate tube, placed between the ineretometer and the flask, when the latter is cooled.

The graduated tube is also provided with an annular trough which serves as a trap and catches the liquid condensed in the upper part of the tube, conveying it to the condenser, thus making the increase of volume in the tube much slower than it otherwise would be.

130. "The Action of Substituting Agents on Benzeneazo- β -naphthol." By J. T. HEWITT and S. J. M. AULD.

Bromine added to benzeneazo- β -naphthol suspended in glacial acetic acid furnishes p -bromobenzeneazo- β -naphthol, a result also obtained by Margary (*Gazzetta*, 1883, xiii., 438), who assigned to the substance the melting-point $160-161^\circ$, but which the authors, like Bamberger, find to be $172-173^\circ$. In presence of sodium acetate, such a high temperature is necessary before the bromine will attack the azo-compound that the results obtained lead to no definite conclusion as to the structure of benzeneazo- β -naphthol.

Nitric acid in presence of concentrated sulphuric acid nitrates the azonaphthol in the benzene nucleus (para-position), dilute nitric acid attacks benzeneazo- β -naphthol on warming, giving 1:6 dinitro- β -naphthol as the chief product, and p -nitrobenzeneazo- β -naphthol in smaller amount.

With strong acids, benzeneazo- β -naphthol behaves as a quinone-hydrazone; with dilute acids (nitric) or weak acids (acetic) its reactions are more those of an azonaphthol.

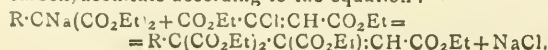
131. "The Condensation of Dimethylaminobenzaldehyde with β -Naphthol." By J. T. HEWITT, A. J. TURNER, B.Sc., and S. W. BRADLEY.

When hydrochloric acid is added to a solution of dimethylaminobenzaldehyde and β -naphthol in cold glacial acetic acid, crystals of the composition $\text{HCl} \cdot (\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_{10}\text{H}_6\text{OH})_2$ are deposited; these darken at about 150° and melt at 215° with decomposition. If, however, a mineral acid be added to a hot glacial acetic acid solution of the aldehyde and β -naphthol, a salt of the corresponding anhydride is produced.

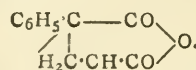
Attempts at oxidation were without result; even bromine does not yield an oxonium salt, but gives the bromide of a bromo-substitution product, $\text{C}_{29}\text{H}_{22}\text{BrON} \cdot \text{HBr}$ (m. p. 196° , uncorr.).

132. "The Action of Ethyl Chlorofumarate on Mono-alkylmalonic Esters." By S. RUHEMANN.

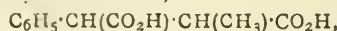
The author finds that, in the presence of sodium ethoxide, ethyl chlorofumarate reacts with the mono-alkyl derivatives of ethyl malonate to yield homologues of ethyl carboxyaconitate according to the equation:—



The quantity of the unsaturated ester which is produced is small, and decreases as the radicle in the substituted malonic ester increases. Of several homologues prepared, the author has studied especially ethyl phenylcarboxyaconitate, $\text{C}_6\text{H}_5 \cdot \text{C}(\text{CO}_2\text{Et})_2 \cdot \text{C}(\text{CO}_2\text{Et})\text{CH} \cdot \text{CO}_2\text{Et}$, and finds that, on hydrolysis, it loses two molecules of water, and yields a compound, $\text{C}_{11}\text{H}_8\text{O}_3$, which is the anhydride of a dicarboxylic acid. This anhydride is not an unsaturated compound, but a derivative of trimethylene having the formula—



On reduction with sodium amalgam, this compound yields s -phenylmethylsuccinic acid,—



(m. p. 193°), which is identical with the acid described by Zelinsky and Buchstab (*Ber.*, 1891, xxiv., 1876).

133. "Di-sec-octyl Tartrate and Di-sec-octyl Dibenzoyl Tartrate." By J. McCRAE.

Di-sec-octyl tartrate was prepared from ethyl octyl tartrate and octyl alcohol by the hydrochloric acid method. It is an oil which boils at 225° (20 m.m.), and has $[\alpha]_D^{18} = +7.06^\circ$. The dibenzoyl derivative was prepared by acting on the ester with excess of benzoyl chloride, and was purified by precipitation with water from an alcoholic solution. It is an oil with $[\alpha]_D^{25} = -43.94^\circ$. The rotations of these two compounds are compared with those of other tartaric esters.

134. "Glycogen from Yeast." By A. HARDEN and W. J. YOUNG.

The glycogen of yeast was extracted by grinding the yeast with sand, pouring the mass into boiling water, and purifying the glycogen by a combination of the methods of Clautriau and Pflüger. Expressed yeast juice was employed. The glycogen, free from ash and nitrogen, was compared with glycogen extracted by Pflüger's method from rabbit liver and from oysters.

All three samples, dried at 100° in a vacuum over phosphorus pentoxide, were found to have the composition $\text{C}_6\text{H}_{10}\text{O}_5$ and not $6\text{C}_6\text{H}_{10}\text{O}_5 + \text{H}_2\text{O}$. Glycogen dried at 100° in air always retained a certain amount of water.

The specific rotations were found to be, rabbit glycogen, $[\alpha]_D^{15} = +191.1^\circ$; oyster glycogen, $[\alpha]_D^{15} = +191.2^\circ$; yeast glycogen, $[\alpha]_D^{16.5} = +198.3^\circ$.

In view of the low concentrations of the solutions rendered necessary by their opalescence, this difference cannot be considered as characteristic.

The glycogen from yeast appears to be identical with animal glycogen in composition and optical activity. Slight differences appear to exist in its behaviour towards dilute acids, in the reaction with iodine, and in the opalescence of the aqueous solutions, but these are also exhibited by glycogens derived from various animal sources.

135. "The Action of Acetylene on the Acetates of Mercury." By E. BURKARD, Ph.D., and M. W. TRAVERS, D.Sc.

The authors have investigated the compounds produced by the action of acetylene on mercurous and mercuric acetates respectively, which were briefly described by the late Dr. R. T. Plimpton (*Proc.*, 1892, viii., 109).

The mercurous compound, which is explosive, has the formula $\text{C}_2\text{Hg}_2\text{H}_2\text{O}$, and resembles the already well-known acetylides of silver, copper, and mercury.

The mercuric compound appears to be a definite basic acetylde of the formula $3\text{C}_2\text{Hg}_2\text{HgO}_2\text{H}_2\text{O}$ or $3\text{C}_2\text{Hg}_2\text{Hg}(\text{OH})_2$; it is non-explosive.

Both compounds yield acetylene when treated with acids, and a mixture of di-iodoacetylene and tetraiodoethylene when treated with iodine. Hence it appears that the oxygen and hydrogen in the compounds are connected with the mercury rather than with the carbon.

136. "The Decomposition of Water Vapour by the Electric Spark." By D. L. CHAPMAN and F. A. LIDBURY.

The experiments described show that when electric sparks are passed through water vapour the decomposition which takes place is considerable. The products of decomposition are partly separated from one another, and take up different positions in the tube. The separation which occurs cannot be entirely accounted for by electrolysis for the following reasons:—

1. Hydrogen collects at both electrodes and oxygen in the middle of the spark gap.

2. The hydrogen which collects at the cathode is very largely in excess of that required by Faraday's law.

137. "The Chlorination of the Dichlorotoluenes in presence of the Aluminium-mercury Couple. The Constitution of the Trichlorotoluenes." By J. B. COHEN and H. D. DAKIN.

The six dichlorotoluenes were chlorinated, using the aluminium-mercury couple as carrier. In order to identify the products formed, the six trichlorotoluenes were prepared synthetically, together with their nitro- and dinitro-derivatives and the trichlorobenzic acids which they yield on oxidation. The results show that the six dichlorotoluenes, on chlorination, give five out of the six possible trichlorotoluenes.

138. "The Constitution of the Nitro- and Dinitro-derivatives of the Dichlorotoluenes." By J. B. COHEN and H. D. DAKIN.

The authors have determined the constitution of the nitro- and dinitro-derivatives of the six dichlorotoluenes which they had previously prepared (*Trans.*, 1901, lxxix., 1111). They find that in the case of the mono-substitution derivatives, the chlorine atoms possess a greater influence than the methyl group in determining the position of the entering nitro-group, whilst in the case of the dinitro-compounds the position of the first entering nitro-group appears to be of primary importance in determining the position to be occupied by the second nitro-group, for in all the six dichlorodinitrotoluenes the nitro-groups are in the meta-position to one another.

139. "Iodonium Compounds of the Type IR'R''R''', and the Configuration of the Iodine Atom." By H. PETERS.

Further investigation of the phenyl-*p*-tolylodonium bromocamphorsulphonate described in a previous note (*Proc.*, 1900, xvi., 62) has confirmed the conclusion that it cannot be resolved into salts of enantiomorphously related bases, from which the inference may be drawn that the three iodine valencies are situated in one plane, two of them being symmetrically situated with respect to the third.

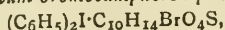
In the preparation of phenyl-*p*-tolylodonium iodide from iodoso-*p*-toluene and iodoxybenzene small quantities of di-*p*-tolylodonium iodide are formed owing to secondary reactions; similarly, the crude phenyl-*p*-tolylodonium iodide, prepared from iodosobenzene and iodoxy-*p*-toluene, contains small quantities of diphenyliodonium iodide. The formation of these subsidiary products is not due to extra-molecular change of the radicals of the phenyl-*p*-tolyl salt, and it is shown that the latter is really the salt of a mixed iodonium base.

Phenyl-*p*-tolylodonium nitrate, $\text{Ph}(\text{C}_6\text{H}_4\cdot\text{Me})_2\text{I}\cdot\text{NO}_3$, crystallises in prisms melting at 117°. The chloride, $\text{Ph}(\text{C}_6\text{H}_4\cdot\text{Me})_2\text{I}\cdot\text{Cl}$, crystallises in needles, and melts at about 193°.

Di-*p*-tolylodonium iodide, $(\text{C}_6\text{H}_4\cdot\text{Me})_2\text{I}\cdot\text{I}$, forms well-defined, octahedral crystals and decomposes at 143–153°.

Di-*p*-tolylodonium bromocamphorsulphonate, $(\text{C}_6\text{H}_4\cdot\text{Me})_2\text{I}\cdot\text{C}_{10}\text{H}_{14}\text{BrO}_4\text{S}$, crystallises in needles melting at 185–186°; it is sometimes obtained in hydrated dodecahedra, very like the crystals of the corresponding salt of the mixed base.

Diphenyliodonium bromocamphorsulphonate,—



forms hydrated dodecahedra, the anhydrous salt melting at 165–168°.

140. "Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds." Part II. By G. T. MORGAN, D.Sc.

Mixed diazoamines containing a naphthalene nucleus are readily obtained from the diazotised *o*- and *m*-nitranilines and 1-chloro- β -naphthylamine. The properties and reactions of several are described in detail in the paper.

141. "Observations on the Phenomena and Products of the Decomposition of Normal Cupric Acetate when Heated." By A. ANGEL and A. V. HARCOURT.

The authors give a summary of the numerous researches on this subject. One phenomenon which had not been noted previously is the formation of a bright coating of copper in the test-tube in which the salt $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\cdot\text{H}_2\text{O}]$, is heated. As this salt does not fuse this must be due to a gaseous compound of copper, proved by the authors to be cuprous acetate, which volatilises at about 200°, and forms, especially when sublimed in hydrogen, feathery white crystals.

The salt was heated generally in a tube in an oil-bath, and kept nearly vacuum by a Sprengel pump, and the gases collected. These were found to consist wholly of the oxides of carbon in approximately the ratio $4\text{CO}_2:\text{CO}$. The liquid products consisted of water and acetic acid with a trace of acetone. The fixed residue is of a paler or deeper red brown colour, and consists of metallic copper mixed with a bulky black substance, the composition of which may be represented by the formula $\text{C}_{11}\text{H}_4\text{O}_4$.

142. "The Resolution of β -Hydroxybutyric Acid into its Optically Active Components." By A. MCKENZIE.

In a preliminary note (*Proc.*, 1901, xvii., 213), the author mentioned that he had obtained *l*- β -hydroxybutyric acid from the inactive acid by aid of the quinine salt.

The *d*-acid has since been isolated by means of the strychnine salt, the solvent being ethyl acetate. It was found that for it $[\alpha]_{\text{D}}^{10} = +24.3^\circ$ ($c = 2.226$).

Change of concentration has little influence on the value for the specific rotation of the acid (Magnus-Levy) and the salts are active in the same sign as that of the acid but to a less degree. In these respects, β -hydroxybutyric acid differs from most other aliphatic oxy-acids.

When the *l*-acid is heated at 100°, it is partly converted into an anhydride.

When the inactive potassium and sodium salts were respectively injected subcutaneously into dogs, the author found from examination of the urine (1) that acetoacetic acid and acetone were present, (2) that a small portion of the β -hydroxybutyrate was unattacked, and (3) that this product was laevorotatory.

Partial resolution of the acid was also obtained by esterification with *l*-menthol and *l*-borneol.

143. "The Rate of Decomposition of Diazo-compounds. Part I. Diazo-compounds of the Benzene Series." By J. C. CAIN and F. NICOLL.

The decomposition of an aqueous solution of a diazo-salt is in most cases a simple monomolecular one, conforming to the expression—

$$C = \frac{1}{t} \log \frac{A}{A-x}.$$

The authors have measured the rate of decomposition of diazo-salts from various bases, and find that at temperatures between 20° and 60° the diazo-salts from aniline and the toluidines conform to the above law, thus confirming some results of Hantzsch at 25° (*Ber.*, 1900, xxxiii., 2517), but being quite opposed to the work of Hauser and Muller at 40° and 64° (*Bull. Soc. Chim.*, 1892, [iii.], vii., 721; 1893, ix., 353).

The authors maintain that the assumption by the latter chemists of a specific "retarding action" of the phenol formed cannot be upheld.

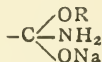
A table of constants of the diazo-salts from eight amines shows the very great stability of the diazo-salts from substances containing an acid group (NO_2 or SO_3H).

The diazo-salt from *p*-amidoacetanilide follows the law only in acetic acid solution, as in presence of mineral acid the acetyl group is saponified.

Of the tetrazo-salts of the diamines, only that from dichlorobenzidine follows the law. The others give in the case of the tetrazo-salts from benzidine and tolidine diminishing, and in the case of that from dianisidine, increasing, values for C_{∞} , pointing to the probability of the formation of an intermediate substance containing still a diazo-group.

144. "Studies upon the Action of Sodamide and Acetyl Substituted Sodamides upon Organic Esters." By A. W. TITHERLEY, D.Sc., Ph.D.

Sodamide appears to form addition compounds containing the grouping—



when allowed to act on esters in benzene solution if the temperature is kept low. On warming, further action at once takes place, which varies according to the nature of the ester. With esters of benzoic and other purely aromatic acids, an alcohol splits off and a substituted sodamide results.

With esters of fatty and phenyl aliphatic acids, the final result of the reaction is a condensation effected on very similar lines to those brought about by sodium ethoxide, and probably by a similar mechanism.

Phenyl benzoate behaves quite differently from the ethyl ester in giving sodium dibenzamide and phenoxide, and the reaction proceeds with great readiness. Ethyl oxalate gives an intermediate product which with water yields sodium oxamate.

The action of sodamide with ketones is very different in the aliphatic series when condensations are brought about from that in the pure aromatic, where there is no action. Acetone with sodamide gives, in presence of benzene after a vigorous reaction, a jelly consisting essentially of the sodium derivatives of the enolic forms of mesityl oxide, phorone, and isophorone.

The interaction of acyl-substituted sodamides and esters depends largely on the nature of both these substances, which, if aliphatic, induce various complex changes. In the pure aromatic series, a simple definite change occurs which conforms approximately to the reversible system $R \cdot CO \cdot NHNa + R' \cdot CO_2R' \rightleftharpoons (R \cdot CO)_2N \cdot Na + R' \cdot OH$, but in all probability the mechanism of the reverse reaction is more complex.

The reaction is capable of modification in numerous ways, and the acyl-substituted sodamide may be prepared from the amide and alcoholic sodium ethoxide, or (best) from sodamide. A very good yield of dibenzamide is obtainable from sodium benzamide and ethyl benzoate.

NOTICES OF BOOKS.

Directions for Laboratory Work in Physiological Chemistry; for the Use of Students in the University and Bellevue Hospital Medical College. By HOLMES C. JACKSON. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1902. Pp. vi.-62. 8vo.

THIS well-devised little volume contains the usual tests and simple experiments made in giving instructions to classes on the following subjects:—Carbohydrates, fats, proteins (general, simple, and compound), albumenoids, muscular tissue, bone, digestion (salivary, gastric, and pancreatic), bile, blood, milk, and urine in all its aspects.

The directions for experimental work are terse and lucid; they assume a general knowledge of the subject, and the method of treatment necessitates consultation of some standard text-book of physiological chemistry. Neither on the title-page nor in the modest preface is any particular book named, but occasional reference is made in the text to the work by Olof Hammarsten, translated

from the German by John A. Mandel, a third edition of which was issued in 1899 by the publishers of the work under review. Dr. Mandel is Professor of Physiological Chemistry in the same institution as the author of this book. Although prepared for the special service named, the work will be found helpful elsewhere.

Occasional interrogation points (within parentheses) inserted in the text direct the attention of students using the volume to consideration of the significance of a reaction or the nature of a product; this simple expedient replaces the questions which sometimes disfigure the pages of text-books, and which frequently seem inane.

The customary designation of special tests by the names of those first announcing them leads to possible difficulty in their application, but the author has avoided this by briefly describing each test. In most cases simplification of language results, but in others this is questionable; the use of glacial acetic acid and concentrated sulphuric acid in examining albumin solutions is hardly simplified by calling the method "Adamkiewicz test," though it is briefer.

The book is well printed, but lacks an index; it is interleaved with blank pages for notes.

Lead Smelting: The Construction, Equipment, and Operation of Lead Blast-furnaces, and Observations on the Influence of Metallic Elements on Slags, and the Scientific Handling of Smoke. By MALVERN WELLS ILES. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1902. Pp. viii.-228. 12mo. Illustrated.

DR. ILES condenses in this volume the results of twenty years' practical acquaintance and successful experience in the smelting of lead; he remarks that most of the literature that precedes him emanates from students of chemistry and metallurgy well versed in the theories of these sciences, but who have not enjoyed the advantage of personal contact with the practical problems confronting lead smelters. Dr. Iles does not undervalue the importance of a profound knowledge of theories, but believes that the experience gained in applying the theories is the prime factor in achieving financial success; he further writes of his book as follows:—

"Without attempt at literary embellishment, and with perhaps censurable disregard for niceties of diction, I go directly to the pith of the subject. My endeavour shall be to give novelty to that which was old, condensation to that which was diffuse, perspicacity to that which was obscure, and accuracy to that which was recondite. I shall attempt truthfully to relate what *has been* and *is*."

This undertaking is fully carried out with a wealth of detail based on experience that makes the volume a rare one. The author devotes the first hundred pages to lead blast-furnaces, their construction, working, and supervision, as well as the method of calculating charges, making daily reports, and checking errors.

In a valuable chapter the "metallurgical results" are discussed; the importance of a "bag-house" is shown, as well as of "slag-settlers," whereby 70 per cent of the silver previously lost in the slag is saved.

Every chapter abounds in records of actual experiments, many pages bristle with figures; the scientific handling of smoke, the influence of metallic elements, the use of roasting-furnaces, antimonial lead as found in the western part of the United States; these form separate chapters of this intensely practical volume.

The book is illustrated with drawings of furnaces obviously accurate, and concludes with an uncommonly full index.

H. C. B.

The Earth in Relation to the Preservation and Destruction of Contagia. By GEORGE VIVIAN POORE, M.D. (Lond.), &c. London, New York, and Bombay: Longmans, Green, and Co. 1902. Pp. 257.

THIS volume is made up of the Milroy Lectures delivered by the author at the Royal College of Physicians in 1899, to-

gether with other papers on sanitation, an Address to the Royal Medical and Chirurgical Society, &c., and its chief object appears to be to advocate the direct application of dung to the soil. The enormous waste of nitrogen which is continuously going on in all our great cities, owing to our modern methods of sanitation, by which sewage is discharged into the sea and lost, is well known, and has been the subject of much discussion and serious thought. Dr. Poore urges the direct application of such matter to the soil itself, and he brings forward many arguments in its favour, backed up by practical instances of its efficacy.

There is a great deal to be said on both sides; there can be no doubt that owing to the drying action of the wind and sun, many pathogenic microbes are widely disseminated in the form of dust; on the other hand, it is equally certain that enormous numbers of these bacteria are killed by the action of these same agencies.

In the country, quite away from large towns, we do not dispute that this method of getting rid of sewage matter is a convenient and possibly harmless one, but we cannot agree that such a method is to be advocated in proximity to large centres of population.

The author brings forward a number of instances in which this means of sewage disposal has been adopted with no untoward results, but has, on the contrary, been found to answer successfully. There are, however, some points to which we must take exception; on several occasions he mentions China as a good example of this, "the dry" method of sewage disposal, and states that physically and economically they (the Chinese) are "going strong," and are likely to continue; surely it is too much to ask us to take the Chinese as a standard of good sanitation; we are not aware of the actual death-rate in China, but from the periodical accounts we receive of deadly epidemics by which even millions of persons are swept off, we cannot accept this example as a proof of the efficacy of the system from the sanitary point of view.

It may be that if the sewage had not been utilised in this manner the inhabitants would have died of starvation, or that the population would not have become so dense; but this is quite another question.

Another point to which we must draw attention is Dr. Poore's description of his garden and the well in the middle of it. This garden is a little over 1 acre in extent, and is manured with the daily faecal matter and house refuse from 100 persons. We quite believe that the practical gardening results are excellent; but in the middle of this garden there is a shallow well, the bottom of which is only five and a half feet from the surface of the ground, and though from its construction no water can enter the well except through the bottom, the author drinks the water without any hesitation or misgiving, because he knows that there are no leaking sewers or cesspools in the immediate neighbourhood! Why, the whole garden is little better than a cesspool! The author admits that his well has retrogressed in bacterial purity, but maintains that this retrogression is caused by insects, such as wood-lice and spiders, which he found under the cover of the well. This is certainly a case of "straining at a gnat and swallowing a camel."

The author then asks, "I wonder if bacteria of the coli group are found in wood-lice, spiders, and water-fleas?" "I wonder what is the life history of a water-flea?" Surely the answers to such simple questions as these could have been ascertained without difficulty.

However, apart from a rather pronounced leaning towards the "dry method" and earth-closets, there is much in this volume of interest and value. The connection between various diseases and the soil as a possible means of contagion has been thoroughly examined.

With regard to contagion from milk, the author does not bind himself to any definite opinion, but he is inclined to think that city children will be improved on the whole by giving them as much new milk as they can take.

The Cyanide Process for the Extraction of Gold; and its Practical Application on the Witwatersrand Goldfields and Elsewhere. By M. EISSLER. Third Edition. Revised and Enlarged. London: Crosby Lockwood and Son. 1902. Pp. 184.

THE result of the additions due to the extension of, and improvements made in, the cyanide process is an increase of about forty pages of new matter in this volume, with some additional illustrations.

We are glad to see that the demand for books on this subject is increasing; there is no doubt that the cyanide process has been the saving of many a mine. It is only free gold that is caught on the plates, and even then it must not be in too finely divided a state; but with the advent of this process practically all the gold in the ore can be recovered, leaving only a few grains in the tailings; in fact, many heaps of tailings which were looked upon as of no worth whatever have become, since the introduction of cyaniding, a very valuable and important asset.

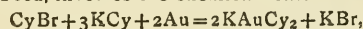
As the successive editions of this book are following so rapidly, we need not add much to our remarks made on the former editions; the value of this work is shown by its success. An important addition, however, has been made in the chapter on "The Treatment of Sulpho-Telluride Ores"; this class of ore occurs in considerable quantities in some of the Australian goldfields, and many mines depended for their very existence on the discovery of a practical method for the extraction of the gold.

In the Kalgoorlie district of Western Australia the Diehl process seems to be the most prominent; after passing under the stamps, the pulp is run over concentrators, and the tailings are ground to such a fineness that they will pass through a sieve carrying 220 holes to the linear inch. After settling and drawing off the excess of water, the pulp is agitated with cyanide of potassium and bromocyanide for twenty-four hours; the gold solution is then separated by filter-presses, and sent to the zinc boxes for reduction. The concentrates are roasted in an automatic furnace, and then ground very fine and treated in the same manner as the bulk of the ore.

The Marriner process consists of dry crushing, roasting, and extraction of the gold by the wet cyanide method; the extraction averages 92½ per cent.

The Riecken process for treating telluride and sulphide ores is an electro-chemical system for the recovery of the precious metals from ores by a single operation without filtration.

The bromo-cyanide process, better known as the Sulman-Teed, involves the chemical reaction—



and the advantage claimed for it over the ordinary cyanide process is its great superiority in "potential" cyanide. The works for treatment by this process do not differ from the ordinary cyanide works. The consumption is 1 lb. of potassium cyanide and 0.33 lb. of cyanogen bromide per ton of ore treated, and the extraction is said to be 90 per cent.

The salient features of another process known as the Cassel-Hinmann are the conversion of the bromine into such a form that it can be shipped as a common salt, requiring only solution in water to make it ready for use; leaching in open vats without creating noxious fumes; the generation of nascent bromine in the interstices of the pulverised ore; the recovery of the bromine, and the ease and completeness of the precipitation of the gold from solution.

The book is of great practical value, and should be in the hands of all gold-mine managers and engineers, while it would not be amiss if directors were to make themselves familiar with its contents.

Institute of Chemistry.—The President's Soirée will take place at the Galleries of the Royal Society of British Artists, Suffolk Street, Pall Mall, on Wednesday, December 10th, at 8.30 p.m.

CORRESPONDENCE.

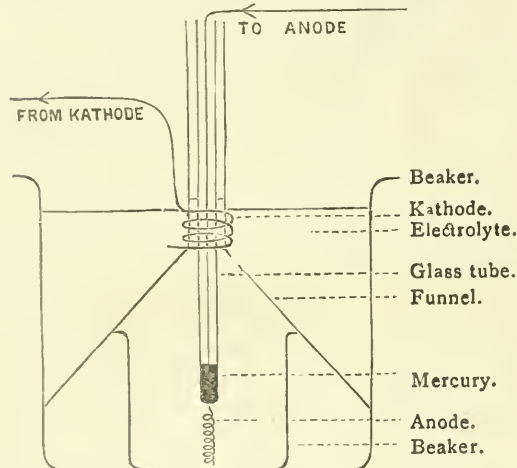
POTASSIUM PERSULPHATE.

To the Editor of the Chemical News.

SIR,—The following is a description of a simple method of quickly preparing some potassium persulphate electrolytically.

The writer used a 400 c.c. beaker. In it he placed a 50 c.c. beaker to receive the deposited persulphate. Over the 50 c.c. beaker was placed a funnel. Through the neck of the funnel was passed a narrow glass tube having a small piece of fine platinum wire fused in to serve as anode. The anode was connected to the circuit by mercury inside the glass tube.

The kathode consisted of two or three turns of platinum wire round the neck of the funnel.



The electrolyte consisted of saturated potassium sulphate in sulphuric acid of density 1.2.

A current of 1.5 ampères was passed through a lamp resistance.

The salt began to deposit after about ten minutes. The temperature was kept at about 14° C.

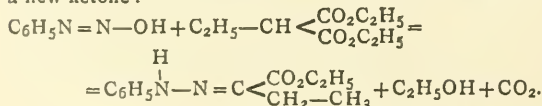
Dr. Karl Elbs gives a good description of persulphate preparations in his recently published book of Electrochemical Preparations.

The apparatus here described is a modification of a test-tube method which he gives.

"S. C." probably had the solution in the porous pot too dilute, and allowed it to get above 20° C., since he used a current of 4 ampères.—I am, &c.,

L. A. G.

Action of the Substituted Malonic Ethers on the Diazoic Chlorides.—M. Favrel.—In the action of the methylmalonate of ethyl on the diazoic chlorides, the methyl group remains fixed to the central carbon, and at the same time there is an elimination of CO₂ and of methylic alcohol. Ethylmalonate of ethyl reacting in the same manner on the diazoic chlorides gives hydrazones of a new ketone:—



Action of Acetylacetone and of its Derivatives of Substitution on the Diazoic and Tetrazoic Chlorides.—M. Favrel.—The author describes a number of bodies prepared by the above means, and gives their analyses and formulæ.—*Bull. Soc. Chim.*, Series 3, xxvii., No. 8.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

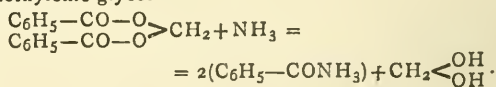
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 17, October 27, 1902.

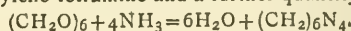
Synthesis of the Anhydrous Hydrosulphites of the Alkalis and the Alkaline Earths.—Henri Moissan.—Sulphurous anhydride at ordinary temperatures and under certain conditions of pressure reacts on the hydrides of the alkali and alkaline earthy metals in such a manner as to form anhydrous hydrosulphites. This synthesis takes place with an evolution of hydrogen and according to the following equation:— $2\text{KH}+2\text{SO}_2=\text{K}_2\text{S}_2\text{O}_4+\text{H}_2$. All the hydrosulphites are soluble in water and possess energetic reducing properties, identical with those which Schutzenberger noticed for the hydrated sodium hydrosulphite. In all cases they are produced by direct union of sulphurous anhydride and the metal, hydrogen being liberated. The syntheses of these anhydrous compounds verify M. Berthsen's formula for the hydrated sodium hydrosulphite.

Volumetric Estimation of Tannin and Analysis of Woods and Tannic Extracts.—Albert Thompson.—Tannin when in presence of solutions of caustic alkalis, such as soda or potash, rapidly absorbs oxygen. The author's estimation therefore depends on the following conditions:—(1) Hydrogen peroxide dissociates totally into water and oxygen under the influence of chemically pure lead peroxide and in presence of a concentrated solution of soda or potash. The lead peroxide should be obtained by the treatment of pure minium with nitric acid. (2) The oxygen thus set free is rapidly absorbed by the tannin when the latter is added to the alkaline hydrogen peroxide before the addition of the lead oxide. (3) The tannin being once saturated, the dissociation of the peroxide continues as if the former body were not present, and all the excess oxygen is liberated. (4) 1 gm. of pure anhydrous tannin absorbs 20 c.m. of oxygen at 0° and 760°. (5) Finally, the tannin is soluble in alcohol at 90°, whilst the greater part of the mineral and peptic substances which accompany it are insoluble. The results obtained represent the whole of the tannin which the skin assimilates.

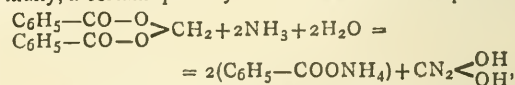
A New Compound of the Group of Hexamethylene-tetramine.—Marcel Descudé.—Methylene-dibenzoate behaves towards ammonia gas in the same way as the ether salts. One portion forms benzamide, the other methylenic glycol—



This unstable glycol at once decomposes into water and formic aldehyde, which complicates the reaction. The formic aldehyde reacts on the excess of ammonia to give hexamethylene-tetramine and a further quantity of water.



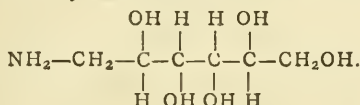
Finally, a certain quantity of the dibenzoate is saponified.



and when the action is complete a mixture of benzamide, ammonium benzoate, and hexamethylene tetramine is present.

A New Base derived from Galactose.—E. Roux.—In a preceding paper the author stated that by reducing sugar oximes he obtained polyalcoholic bases, and one of these, glucamine, he described. The same method applied to the oxime of galactose gives another base, isomeric with the preceding, which is called by analogy galacta-

mine. Its general properties are similar to those of the glucamine already described, and its formula is—



This substance is in the form of a colourless mass of crystalline appearance, very soluble in water, and but slightly soluble in boiling alcohol. It melts at about 139°, and on analysis gives numbers corresponding to the formula $\text{C}_6\text{H}_{15}\text{NO}_5$. Its rotatory power in a 10 per cent solution is -2.77° without multirotation. Its action on metallic salts is similar to that of glucamine, and it does not give a crystalline compound with copper sulphate. It is a strong base which will displace ammonia.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 8.

Aluminate of Barium used as a Disencrustant.—G. Arrth.—This product is obtained from sulphate of barium and bauxite. A "frit" is formed, which gives up to water a soluble portion containing alumina and baryta, and leaves an insoluble residue strongly charged with peroxide of iron. The solution is what is used commercially, and the author has made a number of experiments with a view to obtaining some practical hints as to the best manner of using it. He found that the solution as supplied, gives a white deposit, even when kept closely stoppered, and this deposit goes on forming for at least two months, and its strength drops from 5° B. to 4° B. The solution is used principally with waters containing sulphate of lime before entering the boiler, and the reaction is generally admitted to be $\text{BaO} \cdot \text{Al}_2\text{O}_3 + \text{CaO} \cdot \text{SO}_3 = \text{BaO} \cdot \text{SO}_3 + \text{CaO} \cdot \text{Al}_2\text{O}_3$, both compounds formed being equally insoluble. However, this reaction does not agree with what has been observed in practice, viz., that it requires considerably less baryta than is present according to the equation to purify a given water; that is to say, the decomposition is not effected molecule for molecule between the baryta and the sulphuric acid present. The author has observed that no matter what proportions of sulphate of lime and aluminate of baryta are present, after the reaction there is always lime in the precipitate and in the liquid in which the latter is formed. The precipitate is never formed exclusively of sulphate of barium and aluminate of lime. As a result of experiments he found that it is quite possible to precipitate a given quantity of sulphate of lime with a theoretically insufficient amount of aluminate of barium, but the liquid left after the operation is never quite free from soluble compounds.

Derivatives of β -Methylcyclohexanone.—L. Téty.—The author has obtained a new secondary product of β -methylcyclohexanone by condensation, viz., benzylidene- β -methylcyclohexanone; its composition is $\text{C}_{14}\text{H}_{20}\text{O}_2$. Oxidation of this body by permanganate of potassium gives exclusively benzoic and β -methyladipic acids. Reduction of benzylidene-methylcyclohexanone by sodium amalgam gives benzyl-methylcyclohexanone.

Action of Malonic Ethers on the Diazoic and Tetrazoic Chlorides.—M. Favrel.—The author finds that the action of the tetrazoic chlorides on the malonic ethers is comparable with that of the same ethers on the diazoic chlorides. In both cases there is elimination of water, and the formation of bodies having the composition of the corresponding hydrazones.

Action of the Alcoylacetylacetones on the Diazoic and Tetrazoic Chlorides.—M. Favrel.—These experiments were made with methylacetylacetone and ethylacetylacetone; the bodies obtained are described, and their analyses and formulæ given.

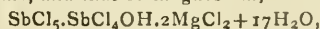
The Detection of the Fatty Acids in Contaminated Waters.—H. Causse.—Already noticed.

New Case of Diastasic Hydrogenation.—M. Pozzi-Escot.—The author has observed that M. de Rey-Pailhade's philothion gives off a notable quantity of sulphuretted hydrogen in the presence of free sulphur; that this philothion gives up hydrogen to selenium and phosphorus; that the action of hydrogenases on oxydases are reciprocal, and that this latter fact explains the destruction of the α -oxydase during the fermentation of wine.

Some Lecture Experiments.—F. Bodroux.—An intimate mixture is made of dry magnesium filings with its own weight of pulverised iodine, so as to obtain a homogeneous powder. No reaction takes place; but if a few drops of water are allowed to fall on the mixture, each one causes a violent reaction at the point of contact. Iodide of magnesium is formed, and the disengagement of heat is such that a portion of the iodine is volatilised. The same phenomenon is observed if we use zinc powder with two parts of iodine; but the most brilliant experiment is with aluminium. Six grms. of iodine and 1 grm. of aluminium powder are intimately mixed in a mortar, and a drop of water dropped in; the reaction takes place immediately; a torrent of iodine fumes comes off, the point of contact becomes inflamed, and the whole mixture burns with a yellow flame. The residue consists almost entirely of alumina. The reaction is explained in the following manner:—The drop of water causes the formation of iodide of aluminium at the point of contact. This formation is accompanied by the evolution of sufficient heat to volatilise the iodide formed; now the vapour of this compound is spontaneously inflammable in the air, and produces alumina, setting the iodine free. The reaction spreads, the iodide of aluminium formed is destroyed immediately; all the iodine is volatilised, and the whole of the metal transformed into oxide.

MISCELLANEOUS.

The Double Salts of Pentachloride of Antimony.—R. F. Weinland and Fr. Schlegelmilch.—In a similar manner to SnCl_4 perchloride of antimony easily forms chlorantimonates; however, the formulæ are more complicated since the salts formed are rather basic. One molecule of SbCl_5 and half a molecule of the other chloride are dissolved in a sufficient quantity of warm, 15 per cent, HCl; the yellow liquid formed gives crystals on the double salt when cooled; with magnesium and calcium the cooling must be considerable. The chlorantimonates are of a pale greenish-yellow colour, and are deliquescent with the exception of the ammonium salt; they are decomposed by water, especially when heated, giving antimonous acid. When calcined they form H_2O , HCl and SbCl_3 ; the chloride and the antimonate of the metal remain. The potassium salt has the formula $\text{SbCl}_5 \cdot \text{SbCl}_4(\text{OH}) \cdot 2\text{KCl}$, and forms rhombic plates; the ammonium salt has a similar formula and appearance. The calcium salt, $\text{SbCl}_5 \cdot \text{SbCl}_4(\text{OH}) \cdot \text{CaCl}_2 + 9\text{H}_2\text{O}$, occurs in long prisms, and that of magnesium,—

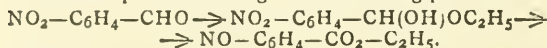


in long prisms or plates.—*Berichte*, vol. xxxiv., p. 2633.

Subchloride of Uranium.—F. Mylius and R. Dietz.—The solution of subchloride of uranium obtained by dissolving uranic acid in hydrochloric acid, after concentration on the water-bath and remaining in the desiccator, gives yellowish-green prisms which are fluorescent, very deliquescent and soluble in water, alcohol, and ether (1 portion in 0.134 part of water at 18°); the saturated aqueous solution is syrupy and denser than glass ($D=2.74$). The salt is the hydrate, $\text{UO}_2\text{Cl}_2 + 3\text{H}_2\text{O}$; its solutions have an acid reaction. If concentrated at 100°, hydrochloric acid is given off, with partial hydrolysis, and on cooling the syrupy liquid we obtain very small citron-yellow needles, non-deliquescent, very soluble in water, less soluble in alcohol than the

original salt, and having a slightly acid reaction. This new salt is $\text{UO}_3 \cdot \text{HCl} + 2\text{H}_2\text{O}$ or $\text{UO}_2 \cdot \text{OH} \cdot \text{Cl} + 2\text{H}_2\text{O}$; it can be compared to $\text{SO}_2 \cdot \text{OH} \cdot \text{Cl}$ with regard to $\text{SO}_2 \cdot \text{Cl}_2$, and may be called chlorouranic acid. However, pure water does not hydrolyse it, but this result is attained by NO_3Ag , which precipitates the whole of the chlorine from the solution; the filtered liquid is yellow and astringent, it precipitates albumin, and its reaction is very slightly acid. An excess of the silver salt must not be used. In this manner we obtain a soluble, colloidal uranic acid, fairly stable at 0° , but at the ordinary temperature depositing, in a few days, a yellow body which is $\text{UO}_2\text{H}_2 + \text{H}_2\text{O}$ or UO_2H_4 , or again $\text{UO}_2(\text{OH})_4$, orthouranic acid; we may remark that by the addition to this formula of 1 or 2 molecules of hydrochloric acid, we obtain the two salts already described.—*Berichte*, vol. xxiv., p. 2774.

Chemical Action of Light.—G. Ciamician and P. Silber.—In the absence of any solvent, or in the presence of a neutral solvent, such as benzene, ether, or acetone, nitrobenzaldehyde is transformed into G. Fischer's nitrosobenzoic acid in the presence of light; if heated to 180° this substance blackens, and at $205-210^\circ$ it is decomposed. In alcoholic solution *o*-nitrobenzaldehyde gives ether and the above mentioned acid; as this acid does not combine directly with alcohol it may be supposed that this addition takes place between the aldehyde and the alcohol in such a manner that the complete reaction should take place according to the following plan:—



Thus we obtain in alcoholic solution the ether of *d*-nitrosobenzoic acid in colourless crystals, fusible at $120-121^\circ$. With methylic alcohol we get the corresponding methylic ether fusing at $152-153^\circ$. With isopropylic alcohol only the free acid is produced. With the meta- and para-nitrobenzaldehydes we obtain results different to those given by the ortho-derivative; the corresponding nitroso acids are not formed, and the aldehyde remains for the greater part untransformed.—*Berichte*, vol. xxiv., p. 2040.

Separation and Estimation of small Quantities of Potassium in Saline Mixtures.—Van Lent.—When salts of potassium are mixed with a large excess of other salts, particularly those of sodium, which is the case with sea-water, their separation by means of chloride of platinum becomes expensive and uncertain, as is also their separation in the form of perchlorate. In such a case it is advisable to make use of cobaltinitrite of sodium, as recommended by M. de Koninck. The sample being first concentrated and freed from the greater part of the lime and magnesia present, by means of carbonate of soda, the reagent is added, and after standing for six or seven hours at about 50° , the solution is filtered. The potassium in the cobaltinitrite is then estimated in the form of perchlorate or chloroplatinate. In the former case, which is the most to be recommended, the precipitate is dissolved with the ash of the filter, in hydrochloric acid, and treated with perchloric acid, in the usual manner. In the latter case, the cobalt salt is calcined gently, and the oxide washed to extract the nitrite of potassium, which is transformed into chloride. This method, applied to a sample of water from the coast of Holland, gave as result:—0.6245 grm. of chloride of potassium per litre, with 15 grms. of chloride of sodium and 5 grms. of sulphate of magnesia.—*Zeit. Anal. Chem.*, vol. xl., p. 569.

MEETINGS FOR THE WEEK.

MONDAY, 24th.—Society of Arts, 8. (Cantor Lectures) "The Future of Coal-gas and Allied Illuminants," by Prof. Vivian B. Lewes.

WEDNESDAY, 26th.—Society of Arts, 8. "Le Tunnel du Simplon, et la Nouvelle Ligne de Chemin de fer Directe Anglo-Italienne pour l'Orient," by Dr. Gustave Goegg, Professor of Technology at the High School of Commerce, Geneva.

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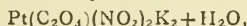
THE CHEMICAL NEWS.

Vol. LXXXVI., No. 2244.

THE COMPLEX SALTS OF PLATINUM. REACTIONS OF THE PLATO-OXALONITRITES.

By M. VÉZES.

PLATO-OXALONITRITE of potassium,—



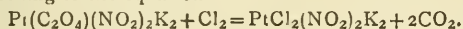
described in a previous paper (*Bull. Soc. Chim.*, Series 3, vol. xxi., p. 481), resembles various other complex salts of platinum in its reactions that I am about to describe now.

I. Action of Chlorine, Bromine, and Iodine.

Chlorine does not appear to form any combination with this salt analogous to that which it gives with the platonitrite of potassium, at least not when working in the wet way. In fact, when we pass a current of chlorine through a solution of the oxalonitrite, kept warm so as to prevent the deposition of the salt, which is very slightly soluble in the cold, no crystalline deposit is observed, while under the same conditions, the platonitrite gives, first of all, an abundant deposit of the plati-dichloronitrite, $\text{Pt}(\text{NO}_2)_2\text{Cl}_2\text{K}_2$.*

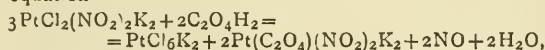
Quite on the contrary, however, the solution undergoes a reaction during the passage of the chlorine, which has the effect of transforming, at least partially, the oxalonitrite into more soluble products, for, when left to stand in the cold it does not give any deposit, in spite of the concentration it has undergone during the operation. It is necessary to concentrate it further to obtain a final deposit; this consists of chloroplatinate mixed with a little unattacked oxalonitrite. The reaction of the chlorine on the oxalonitrite thus appears to be expressed in a simple manner by the equation—

$\text{Pt}(\text{C}_2\text{O}_4)(\text{NO}_2)_2\text{K}_2 + 3\text{Cl}_2 = \text{PtCl}_6\text{K}_2 + 2\text{NO}_2 + 2\text{CO}_2$, unless it forms intermediate products, such as the plati-dichloronitrite, which, it would appear, might be formed according to the equation—



Thus chlorine does not appear to be able to displace the carbon groups of the oxalonitrite without at the same time displacing the nitrogen groups. On the other hand, oxalic acid is able to displace the chlorine from a chloronitrated salt without, at the same time, displacing the whole of the nitrogen; in fact, if we act with an excess of oxalic acid on a solution of plati-dichloronitrite of potassium, a part of this salt is transformed into chloroplatinate with the evolution of nitrous fumes, but the greater portion passes into the state of oxalonitrite, thus keeping the whole of the nitrogen it originally contained.

This transformation can be represented by the equation—

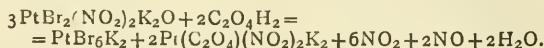


and thus would constitute a means for the preparation of the oxalonitrite from the plati-dichloronitrite of potassium, if it was not so difficult to separate the product obtained from the chloroplatinate with which it crystallises.

* We may remark here that this fact makes untenable the hypothesis encouraged by certain other reactions, according to which plati-oxalonitrite of potassium would be a product of addition, dissociable by water, of the platonitrite and plati-oxalate of potassium; if this were the case, the solution of this salt would contain some platonitrite, and would give this characteristic reaction with chlorine, which, however, does not take place. The hypothesis in question, therefore, should be rejected; further, it is rendered very improbable by the ease with which the plati-oxalonitrite is formed in a solution containing a notable excess of one or the other of these two components.

Bromine gives with plati-oxalonitrite of potassium a reaction analogous to that of chlorine; it transforms the plati-oxalonitrite into bromoplatinate without the formation of either products of addition or intermediate products, such as the plati-dibromonitrite, $\text{PtBr}_2(\text{NO}_2)_2\text{K}_2$. We have simply:— $\text{Pt}(\text{C}_2\text{O}_4)_2\text{K}_2 + 3\text{Br}_2 = \text{PtBr}_6\text{K}_2 + 2\text{NO}_2 + 2\text{CO}_2$.

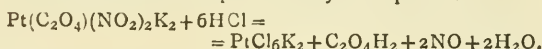
Inversely, the action of oxalic acid on the bromonitrated salts of platinum gives a mixture of bromoplatinate and oxalonitrite. For example, with the plati-dibromonitrite we have:—



Iodine gives analogous results, but less distinctly on account of a possible deposit of platinic iodide which here replaces the bromoplatinate or the chloroplatinate, as well as the reduction of the salt to the state of metallic platinum by the alcohol used as a solvent. Here, again, it is not possible to obtain the plati-diiodonitrite, $\text{PtI}_2(\text{NO}_2)_2\text{K}_2$, from the oxalonitrite; the inverse reaction, on the other hand, is easy.

II. Action of Hydrochloric, Hydrobromic, and Hydriodic Acids.

Hydrochloric acid transforms plati-oxalonitrite of potassium into chloroplatinate without the formation of intermediate products, such as the plati-dichloronitrite. If we use less than six molecules of acid for each molecule of the salt, we obtain by the evaporation of the greenish-yellow liquid formed, a mixture of chloroplatinate and unattacked oxalonitrite, and, at the same time, crystals of oxalic acid, which, with the nitrous fumes given off during the operation, form the secondary products of the reaction. This reaction can be represented by the equation—



Hydrobromic acid causes an analogous transformation, and gives the bromoplatinate, PtBr_6K_2 .

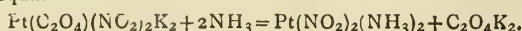
Hydriodic acid gives a reaction differing slightly from the preceding ones, on account of the great stability and insolubility of platinic iodide, PtI_4 . It is, in fact, this body which is precipitated as an abundant black deposit when we heat a solution of plati-oxalonitrite with hydriodic acid. At the same time, nitrous fumes are given off, and the solution contains oxalate of potassium:— $\text{Pt}(\text{C}_2\text{O}_4)(\text{NO}_2)_2\text{K}_2 + 4\text{HI} = \text{PtI}_4 + \text{C}_2\text{O}_4\text{K}_2 + 2\text{NO} + 2\text{H}_2\text{O}$.

If we use a quantity of hydriodic acid, insufficient to precipitate all the platinum in the form of iodide, the filtered solution, after evaporation and cooling, leaves unattacked oxalonitrite. Thus, here again, it is not possible to detect the formation of intermediate products, such as the plati-diiodonitrite.

III. Action of Ammonia.

Ammonia gives immediately a very abundant white precipitate with solutions of the plati-oxalonitrates, as with all the other mixed nitrated salts containing at least two atoms of nitrogen for each atom of platinum; this precipitate has, under the microscope, the appearance of a mass of very fine colourless needles; it is slightly soluble in boiling water, and less so in cold water. When washed, dried, and heated to below a red heat, this body detonates with violence without forming any carbonic gas, or leaving any other residue than platinum free from soluble matters.

These characteristics, as also the estimation of the platinum by calcination with sulphuric acid (calculated, 60.67; found, 60.76), enables us to recognise in this body the nitrite of platosamine, $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$, which was described by Lang (*Journ. f. Prakt. Ch.*, vol. lxxxiii., p. 418), and which is formed in this case according to the equation—



IV. Action of the Metallic Salts.

Plato-oxalonitrite of potassium gives particularly interesting reactions with most of the metallic salts. We have already (*Bull. Soc. Chim.*, Series 3, vol. xxv., p. 157) examined the case in which we react on this body with chloride of barium, strontium, or calcium; we propose now to examine the case of the salts of silver, copper, nickel, lead, and magnesium.

Salts of Silver.—Nitrate of silver, with solutions of plato-oxalonitrite of potassium, gives an immediate deposit of very fine colourless needles, very slightly soluble, especially in the cold; in fact, they are only soluble in about 1000 times their weight of cold water and in 50 times their weight of boiling water. Heated to about 110° , they lose their water of crystallisation; towards 250° they decompose, forming bubbles, and giving off binoxide of nitrogen and carbonic acid gas, at the same time leaving a black residue formed of platinum, silver, and nitrate of potassium. The crystallographical examination, made by M. Dufet, gave the following results:—

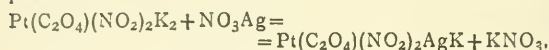
Long prisms, not more than 2 m.m. in thickness, with the facets h_3 (210) and g_1 (010), terminated by a perfect cleavage following the base. Clinorhombic system—

$$a : b : c = 0.8820 : 1 : ?$$

$$\beta = 87^{\circ} 52'.$$

The extinction in g_1 occurs at 6° from the vertical axis in the acute angle of the axes. The plane of the optical axes is perpendicular to g_1 ; the axes seen in g_1 do not extend into the air. In bromised naphthalene of r.6578 index, they form an angle of $2H = 96^{\circ} 22'$ round the normal to g_1 in the plane 6° from the vertical axis.

Analysis gives these crystals the following formula:— $Pt(C_2O_4)(NO_2)_2AgK + H_2O$; thus it is an argento-potassic plato-oxalonitrite resulting from the partial double decomposition:—



Below are the analytical results found for the salt thus obtained:—

I. 1.0745 grms. of material, heated to 110° , lost 0.0350 gm. of water. The dry product, heated to about 300° , lost 0.2413 gm. of carbonic acid and nitric oxide, leaving a residue of 0.7982 gm. This residue, treated with warm water, gave up 0.1897 gm. of nitrate of potassium, containing 0.0734 gm. of potassium; washings with dilute warm nitric acid removed 0.2073 gm. of metallic silver, leaving a residue of 0.4012 gm. of platinum.

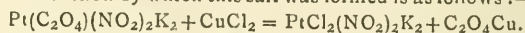
II. 0.5922 gm. of material, heated to about 300° , left a residue of 0.4403 gm., from which were separated 0.1055 gm. of nitrate of potassium containing 0.0409 gm. of potassium, 0.1134 gm. of silver, and 0.2214 gm. of platinum.

III. 0.5868 gm. of material, heated to redness with tungstic acid and copper, gave 23.6 c.c. of nitrogen at 0° and 760 m.m., and 52 c.c. of carbonic gas at 0° and 760 m.m., containing 0.0279 gm. of carbon.

	Calculated.		Found.		
	I.	II.	I.	II.	III.
Pt	194.8	36.08	37.34	37.39	—
Ag	107.9	19.99	19.29	19.15	—
K	39.1	7.25	6.83	6.90	—
2C	24.0	4.45	—	—	4.75
2N	28.1	5.20	—	—	5.05
8O	128.0	23.70	—	—	—
H ₂ O	18.0	3.33	3.26	—	—
$Pt(C_2O_4)(NO_2)_2AgK.H_2O$	539.9	100.00	—	—	—

Salts of Copper.—If we mix two solutions of plato-oxalonitrite of potassium and cupric chloride in equimolecular proportions, the blue liquid obtained, which is first of all limpid, becomes cloudy and soon deposits an abundant bright blue precipitate having a crystalline appearance under the microscope. After boiling for some moments to complete the precipitation, if we separate the

precipitate by filtration and wash it carefully, we find by qualitative analysis that it consists of pure oxalate of copper, and by electrolytic estimation that it contains practically all the cupric chloride used; in an experiment made with 20 grms. of oxalonitrite and 7.2 grms. of hydrated cupric chloride, $CuCl_2 \cdot 2H_2O$, containing 2.7 grms. of copper, the electrolysis of the precipitated oxalate re-dissolved in an excess of oxalate of ammonium, gave 2.6 grms. of copper. The liquid, filtered after the precipitation of the copper as oxalate, is of a golden-yellow colour. When strongly concentrated by slow evaporation it gives yellow crystals of plato-dichloronitrite of potassium, $PtCl_2(NO_2)_2K_2$ (platinum calculated, 44.67; found, 44.79—chloride of potassium calculated, 34.21; found, 34.05—nitrogen calculated, 6.44; found, 6.29). The reaction by which this salt was formed is as follows:—



Thus, we see that the action of chloride of copper on plato-oxalonitrite of potassium gives the same product as the carefully managed action of hydrochloric acid on the platonitrite. This conclusion can be generalised, as it is easy to make certain by reacting on the plato oxalonitrite with another salt of copper such as the sulphate or nitrate.

Certain strong acids, particularly sulphuric and nitric acids, react on the platonitrite under the influence of heat, giving an acid product crystallised in the form of red needles; this is the acid triplatohexanitrite of potassium, $Pt_3O(NO_2)_6K_2H_4 + 3H_2O$ (*Comptes Rendus*, vol. cxvi., pp. 99, 160, and 185).

Now, if we mix equivalent solutions of plato oxalonitrite and sulphate or nitrate of copper, we obtain first of all a bright blue, crystalline precipitate, containing all the copper in the form of oxalate, and the filtrate after concentration deposits an abundance of red needles of this acid triplatohexanitrite. Thus we can say in a general way that the action of a copper salt on plato-oxalonitrite of potassium gives the same product as the carefully managed action of the acid of this salt on the platonitrite.

Salts of Nickel, Lead, and Magnesium.—The same rule appears to apply to the salts of most of the heavy metals. It is in this manner that chloride of nickel gives a solution of plato-dichloronitrite, with a precipitate of oxalate of nickel containing all the metal from the chloride used. Chloride of lead in the same way gives a deposit of oxalate of lead and a solution of plato-dichloronitrite of potassium. Iodide of lead, in spite of the special difficulties resulting from its slight solubility, gave with a precipitate of oxalate of lead a solution of plato-diiodonitrite of potassium, $PtI_2(NO_2)_2K_2 + 2H_2O$. Finally, bromide of magnesium in the same way gave with a deposit of oxalate of magnesium a solution which after concentration gave plato-dibromonitrite of potassium, $PtBr_2(NO_2)_2K_2 + H_2O$ (platinum calculated, 35.84; found, 35.73—bromide of potassium calculated, 43.89; found 43.16—water calculated, 3.32; found, 3.70).

These reactions, which are effected in neutral solution, thus constitute a convenient means for the preparation of the mixed plato-salts of $PtX_2(NO_2)_2K_2$; they furnish products purer than those obtained by the action of the hydracids on the platonitrite, admitting the tendency which all the chloro- or bromo-nitrated compounds of platinum have to form a chloroplatinate or a bromoplatinate when they are heated in an acid solution.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 18.

Analysis of Nine Specimens of Air taken from the Galleries of Mines.—Nestor Gréhan. The author's experiments were conducted in the galleries of a coal mine in process of working. The most noticeable feature of the analysis is the large proportion of formene in such air. The carbonic acid varies between 1 and 1.8 per cent. The proportion of oxygen is perceptibly less than that of normal air.—*Comptes Rendus*, cxxxv., No. 18.

THE ANALYSIS OF LITHOPONE.

By CH. COFFIGNIER.

In a previous paper (*Bull. Soc. Chim.*, vol. xxvii., p. 829) I gave the compositions of a series of lithopones of different manufactures, and the method of analysis used. At the end of this paper I drew attention to a certain number of abnormal results obtained. Among these, *one* only was due to an analytical error in the estimation of the sulphate of barium; all the others require explanation.

Since the publication of my first paper, I have succeeded in obtaining further samples, and thus confirming the first results in such a manner as to show that the results obtained are all to be depended upon. I have also analysed richer samples, containing from 40 to 50 per cent of sulphide of zinc.

I will give now the whole series of analyses which have given me results analogous to those I obtained previously.

Specimens containing 20 to 22 per cent of Sulphide of Zinc.

	E.		A.	
	1.	2.	1.	2.
Moisture	—	0'18	—	0'12
Aqueous extract ..	—	0'32	—	0'24
Oxide of zinc	—	1'50	—	1'53
Sulphide of zinc ..	21'40	19'34	25'40	23'47
Sulphate of barium ..	78'63	78'63	74'40	74'40
	100'03	99'97	99'80	99'76

Specimens containing 26 per cent Sulphide of Zinc.

	E.	
	1.	2.
Moisture	—	0'30
Aqueous extract ..	—	0'34
Oxide of zinc	—	1'34
Sulphide of zinc ..	26'75	24'90
Sulphate of barium ..	73'22	73'22
	99'97	100'10

Specimens containing 29 to 30 per cent Sulphide of Zinc.

	C.		G.	
	1.	2.	1.	2.
Moisture	—	0'14	—	0'18
Aqueous extract ..	—	0'28	—	0'14
Oxide of zinc	—	1'46	—	2'95
Sulphide of zinc ..	30'50	28'68	31'05	27'05
Sulphate of barium ..	61'10	69'10	69'54	69'54
	99'60	99'66	100'59	99'86

Specimens containing 33 to 34 per cent Sulphide of Zinc.

	A.		C.	
	1.	2.	1.	2.
Moisture	—	0'04	—	0'20
Aqueous extract ..	—	0'08	—	0'20
Oxide of zinc	—	1'98	—	0'59
Sulphide of zinc ..	34'60	32'01	37'12	36'40
Sulphate of baryta ..	66'00	66'00	62'73	62'73
	100'60	100'11	99'85	100'12

	D.*	
	1.	2.
Moisture	—	0'08
Aqueous extract ..	—	0'54
Oxide of zinc	—	0'65
Sulphide of zinc ..	20'47	19'40
Sulphate of barium ..	79'20	79'20
	99'67	99'87

* This sample, marked 33 to 34 per cent, was certainly badly taken. It comes in the class 20 to 22 per cent.

Very Rich Specimens.

	A.		A.		A.	
	40 per cent.		45 per cent.		50 per cent.	
	1.	2.	1.	2.	1.	2.
Moisture	—	0'20	—	0'18	—	0'10
Aqueous extract ..	—	0'24	—	0'34	—	0'56
Oxide of zinc	—	2'00	—	2'00	—	2'40
Sulphide of zinc ..	41'27	38'80	45'11	42'37	50'36	47'52
Sulphate of barium	58'35	58'35	54'83	54'83	49'14	49'14
	99'62	99'59	99'94	99'72	99'50	99'72

All these results, obtained with samples from six different makers, show conclusively that the method of analysis is to be depended upon.

The analyses of which I am now about to speak, total up in Column 1 to the figures 96'97 to 98'83; in Column 2, from 97'99 to 98'83. In both these cases the figures obtained are inadmissible.

Now, these results were always obtained with samples from the same maker. This is the first point which attracted my attention.

Lithopone is obtained by precipitating a solution of sulphate of zinc with a solution of sulphide of barium; the precipitate obtained contains oxysulphhydrate of zinc, hydrated oxide of zinc, and sulphate of barium. The action of water on the sulphide of barium obtained by the reduction of the sulphate, gives an oxysulphhydrate of barium and hydrate of baryta. Calcination of the precipitate transforms the oxysulphhydrate into sulphide and the hydrated oxide into oxide; from which it follows that commercial lithopone is a mixture of sulphide of zinc, oxide of zinc, and sulphate of baryta. Thus it is very possible that these types giving abnormal results have not been sufficiently calcined. By taking the zinc soluble in dilute acetic acid to be $Zn\begin{smallmatrix} SH \\ OH \end{smallmatrix}$, instead of ZnO , we get a more likely result, as will be seen from an examination of the following figures:—

	F (22 to 23 per cent).			F (29 to 30 per cent).		
	1.	2.	3.	1.	2.	3.
H ₂ O	—	1'46	1'46	—	1'50	1'50
Aqueous extract ..	—	0'80	0'80	—	0'72	0'72
ZnO	—	3'54	—	—	4'34	—
$Zn\begin{smallmatrix} SH \\ OH \end{smallmatrix}$	—	—	5'02	—	—	6'17
ZnS	26'50	22'28	22'28	31'13	25'87	25'87
SO ₄ Ba	70'75	70'75	70'75	65'95	65'95	65'95
	97'25	98'83	100'31	97'08	98'38	100'21

	F (32 to 34 per cent).			F (40 to 42 per cent).		
	1.	2.	3.	1.	2.	3.
H ₂ O	—	0'86	0'86	—	1'00	1'00
Aqueous extract ..	—	1'16	1'16	—	1'34	1'34
ZnO	—	4'27	—	—	5'92	—
$Zn\begin{smallmatrix} SH \\ OH \end{smallmatrix}$	—	—	6'07	—	—	8'28
ZnS	34'81	29'54	29'54	41'92	34'68	34'68
SO ₄ Ba	62'60	62'60	62'60	55'05	55'05	55'05
	97'41	98'43	100'24	96'97	97'99	100'35

If the analyses in Columns 3 are a little too high, it is really because the whole of the soluble zinc is not in the form of $Zn\begin{smallmatrix} SH \\ OH \end{smallmatrix}$, but partly in this state and partly as ZnO .

It may be remarked that all these types, compared with the preceding ones, give a much higher proportion of moisture and ZnO .

From the point of view of the explanation I have just given, I will give the results of the analyses obtained from two samples sent to me by French makers who were endeavouring to establish the manufacture of lithopone

without calcination. The products they sent me were obtained by means of double decomposition, passing through the filter-press, and drying at about 110° .

	H.			I.		
	1.	2.	3.	1.	2.	3.
H ₂ O	—	2.88	2.88	—	2.66	2.66
Aqueous extract ..	—	0.48	0.48	—	2.02	2.02
ZnO	—	1.66	—	—	1.40	—
Zn<math>\begin{smallmatrix} \text{SH} \\ \text{OH} \end{smallmatrix}>	—	—	2.36	—	—	1.95
ZnS	28.43	26.60	26.60	27.95	26.36	26.36
SO ₄ Ba	67.40	67.40	67.40	66.70	66.70	66.70
	95.83	99.02	99.72	94.65	99.14	99.69

We see that here, as in the preceding cases, the analysis is only satisfactory when we admit that the zinc soluble in dilute acetic acid is in the state of $\text{Zn}<\mathbf{SH}>$. To obtain

an experimental proof of this theory I precipitated a solution of sulphide of barium by chloride of zinc. The washed precipitate, treated with acetic acid at 1 per cent, gave a solution precipitable with sulphuretted hydrogen. During the action of the dilute acetic acid the odour of sulphuretted hydrogen was distinctly observable. All these characteristics were observed when attacking lithopones which had given abnormal analytical results with dilute acetic acid. Taking these observations altogether, it appears to me to be quite evident that the presence of the oxysulphhydrate of zinc will account for the anomalies observed in the analysis of some of the samples.—*Bull. Soc. Chim.*, Series 3, vol. xxvii, No. 18.

CONTRIBUTIONS TO OUR KNOWLEDGE OF YTTERBIUM.*

By ASTRID CLEVE.

(Continued from p. 249).

III. COMPOUNDS OF YTTERBIUM.

Ytterbium Oxide, Yb₂O₃.

FIRST examined and described by Nilson, according to whom it has the high specific gravity 9.175. When perfectly pure the substance is colourless. But probably the least traces of thulium are sufficient to colour the oxide, as the preparations after very strongly heating mostly have a yellow or brownish tinge. The oxide is slowly attacked by acids in solutions, as well as at a red heat. It is quite insoluble in weak acids such as acetic acid.

According to a communication from Dr. Euler, the earth is not radio-active.

Ytterbium Chloride, YbCl₃+6H₂O.

The salt is very soluble and deliquescent. It may be precipitated in crystals by dissolving the oxide in concentrated hydrochloric acid, and saturating with hydrochloric acid gas; it then forms beautiful, clear, tapering prisms. It does not part with any of its water to sulphuric acid or lime, or when heated to 70° . At 100° slow decomposition takes place, and on strongly heating the chlorine is given up altogether.

Analyses.

- 0.9082 grm. of the substance dried at 70° gave on ignition 0.4631 grm. Yb₂O₃.
- 0.7313 grm. of the substance dried over CaO gave 0.8141 grm. AgCl.

	Calculated for YbCl ₃ +6H ₂ O, in per cent.		Found.	
	I.	II.	I.	II.
Yb	173.1	44.66	44.78	—
Cl ₃	106.35	27.44	—	27.52
6H ₂ O	108.12	27.90	—	—
	387.57	100.00		

* From the *Zeitschrift für Anorganische Chemie*, xxxii.

Specific Gravity and Molecular Volume.

1. 1.2550 grms., specific gravity	2.570
2. 1.1056 " " " " " " " " " "	2.580
Mean	2.575
Molecular volume	150.5

Ytterbium Oxychloride, YbOCl.

A substance approximately of this composition was obtained by dissolving the chloride in water and heating in a current of hydrochloric acid gas, first to dryness, and then to a red heat. After some time a white hygroscopic residue was obtained, and was analysed.

- 0.6237 grm. of the substance, after heating before the blowpipe, gave 0.5338 grm. Yb₂O₃.
- 0.8894 grm. of the substance gave 0.6819 grm. AgCl.

	Calculated for YbOCl, in per cent.	Found.	
		I.	II.
Yb	77.08	75.17	—
Cl.	15.79	—	18.95

The analysis shows that the formation of the oxychloride was not quite completed, probably because it had not been heated sufficiently.

Ytterbium Bromide, YbBr₃+8H₂O.

This was prepared in the same way as the preceding salt, which it resembles, though it is still more deliquescent. The solution dries very slowly over lime, giving crystals containing 8 molecules of water.

Analysis of the Pressed Salt.

- 1.0463 grms. of the substance gave 1.0518 grms. AgBr.
- 1.4707 grms. of the substance gave 1.4797 grms. AgBr.
- 0.7621 grm. of the substance gave 0.2686 grm. Yb₂O₃.

	Calculated for YbBr ₃ +8H ₂ O, in per cent.		Found.		
	I.	II.	I.	II.	III.
Yb	173.1	31.07	—	—	30.95
Br ₃	239.88	43.06	42.78	42.81	—
8H ₂ O	144.16	25.87	—	—	—
	557.14	100.00			

The bromides of yttrium and erbium crystallise possibly with the same amount of water (*cf.* Cleve and Höglund, *Bull. Soc. Chim.*, 1872, xviii, 196).

Ytterbium Iodate, Yb₃IO₃+6H₂O (Dried over Sulphuric Acid).

It is produced in the form of a white amorphous precipitate when solutions of iodic acid and ytterbium acetate are mixed. When dried, it gives a snow-white powder.

Analysis.

- 0.9863 grm. of the substance dried in the desiccator gave up 0.0365 grm. of water at 100° .
- 0.3268 grm. of the substance gave, after reduction with SO₂, 0.2852 grm. AgI.

	Calculated for Yb ₃ IO ₃ +6H ₂ O, in per cent.		Found.
	I.	II.	

I	47.23	47.15
2H ₂ O	4.27	3.70 (loss of weight at 100°).

Thus 4 molecules of water remained in combination above 100° .

Ytterbium Periodate, YbIO₅+2H₂O (Dried over Sulphuric Acid).

A white hygroscopic powder, obtained from ytterbium acetate and periodic acid. After having been dried in the sulphuric acid desiccator, it suffers no loss of weight at $100-115^{\circ}$.

Analysis.

0.4521 grm. of the substance dried over sulphuric acid gave, after reduction with SO_2 , 0.2556 grm. AgI.
0.2134 grm. of Yb_2O_3 were precipitated from the filtrate by means of ammonia.

		Calculated for YbIO ₃ +2H ₂ O, in per cent.		Found.
Yb	173.1	41.61		41.46
I	126.85	30.50		30.55
O ₅	80	19.23		—
2H ₂ O ..	36.04	8.66		—
	415.99	100.00		

Corresponding periodates of yttrium (Cleve, *Bull. Soc. Chim.*, 1874, xxi., 345) and samarium (Cleve, "Contributions to the Knowledge of Samarium," *Nova Acta Reg. Soc. Sc. Ups.*, Ser. III., p. 16)—the latter, however, with 4H₂O at 100°—are known.

Ytterbium-platinum Chlorides.

1. $2\text{YbCl}_3 \cdot \text{PtCl}_4 + 22\text{H}_2\text{O}$.

Crystallises from the mixture of the solutions of ytterbium chloride and platinum chloride (the latter in excess) in large transparent rhombic tables of reddish brown colour. The crystals deliquesce in damp air, but crumble in the desiccator, the colour changing to light yellow. At 100°, half the water of crystallisation is given up; below this temperature, the salt dissolves in its water of crystallisation. Its reaction is neutral.

Analysis of the Pressed Substance.

- 0.5424 grm. of the substance gave up 0.0839 grm. of water at 100°, and, after ignition, gave a residue of 0.3524 grm. $\text{Yb}_2\text{O}_3 + \text{Pt}$, of which 0.0820 grm. was platinum.
- 0.5552 grm. of the substance gave 0.3553 grm. $\text{Yb}_2\text{O}_3 + \text{Pt}$, of which 0.2740 grm. was Yb_2O_3 and 0.0813 grm. platinum.
- 0.5557 grm. of the substance gave 0.6354 grm. AgCl.

		Calculated for $2\text{YbCl}_3 \cdot \text{PtCl}_4 + 22\text{H}_2\text{O}$, in per cent.		Found.		
				I.	II.	III.
Yb ₂ ..	346.2	26.80	27.33	27.07	—	—
Pt ..	194.8	15.08	15.1	14.7	—	—
Cl ₁₀ ..	354.5	27.44	—	—	27.20	—
22H ₂ O ..	396.44	30.68	15.47 (loss of H ₂ O at 100°).	—	—	—
1291.94		100.00				
Yb ₂ ·3SO ₄ + Pt..	64.18	64.98	64.00			

2. $2\text{YbCl}_3 \cdot \text{PtCl}_4 + 35\text{H}_2\text{O}$.

Another preparation gave on analysis the above quantity of water.

- 0.6240 grm. of the pressed substance gave 0.3400 grm. $\text{Yb}_2\text{O}_3 + \text{Pt}$, of which 0.2602 was Yb_2O_3 and 0.0798 grm. was Pt.

		Calculated for 2YbCl ₃ PtCl ₄ +35H ₂ O, in per cent.		Found.
Yb ₂		346.2	22.69	22.76
Pt..		194.8	12.76	12.8
Cl ₁₀		354.5	23.23	—
35H ₂ O	. ..	630.7	41.32	—
		1526.2	100.00	
Yb ₂ .3SO ₄ +Pt..		54.33		54.49

Thus both the above salts do not belong to the ordinarily occurring type of platinum double chlorides of rare earths, $\text{R}^{\text{III}}\text{Cl}_3 \cdot \text{PtCl}_4 + n\text{H}_2\text{O}$; where R^{III} may be praseodymium (v. Schéele, "Om Praseodym, &c.," *Inaug. Diss.*, Upsala, 1900, p. 47), samarium (Cleve, "Contributions to the Knowledge of Samarium," p. 10), gadolinium (Benedicks,

Zeit. Anorg. Chem., xxii., 404), or erbium (Cleve, *Bull. Soc. Chim.*, 1874, xxi., 345), but contain $2\text{R}^{\text{III}}\text{Cl}_3$ to each PtCl_4 . The yttrium salt has the composition $4\text{YCl}_3 \cdot 5\text{PtCl}_4 + 51\text{H}_2\text{O}$ (Cleve and Nilson, *Bull. Soc. Chim.*, 1877, xxvii., 209).

Acid Ytterbium Platinum Bromide,
 $\text{YbBr}_3 \cdot 3\text{H}_2\text{Br}_6\text{Pt} + 30\text{H}_2\text{O}$.

It was prepared in the same way as the platinum double chloride, and forms dark red rhombic tables, which are exceedingly deliquescent. The salt has an acid reaction, and decomposes carbonates. A neutral double bromide could not be isolated in this way.

Analysis of the Pressed Substance.

- 0.8078 grm. of the salt gave 0.2540 grm. $\text{Yb}_2\text{O}_3 + \text{Pt}$, of which 0.0951 grm. was Yb_2O_3 , and 0.1589 grm. Pt.
- 0.3438 grm. of the substance gave 0.4494 grm. AgBr.

		Calculated for $\text{YbBr}_3 \cdot 3\text{H}_2\text{Br}_6\text{Pt} + 30\text{H}_2\text{O}$, in per cent.		Found.	
				I.	II.
Yb	173.1	5.80	6.46	—	—
H ₆	6.06	0.20	—	—	—
Pt ₃	584.4	19.59	19.66	—	—
Br ₂₁	1679.16	56.29	—	55.63	—
30H ₂ O ..	540.6	18.12	—	—	—
2983.32		100.00			

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 6, 1902.

Professor McLEOD, F.R.S., Vice-President, in the Chair.

THE CHAIRMAN referred to the great loss which the Society had sustained since its last meeting by the deaths of Sir Frederick Abel and Dr. J. H. Gladstone, two of its Past Presidents, who had been for more than fifty years Fellows of the Society.

Messrs. Garle, Hann, Pollitt, Gill, Moore, and Parkes were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Frederick Alder, 13, Priestwood Mansions, Highgate, N.; Alfred Edward Beanes, Moatlands, Paddock Wood; Herbert Blair, No. 3, General Hospital, Kroonstad; John A. H. Brincker, B.A., M.B., 7, St. Mary's Terrace, Paddington, W.; Vernon Seymour Bryant, B.A., Camborne, Cornwall; Thomas Burnell Carmichael, Parton, Whitehaven; Charles Cockle, Peter Symonds School, Winchester; James Justinian Drought, Johannesburg; Walter Henry Edwards, The Grammar School, Wellingborough; Wilfrid Russell Grimwade, B.Sc., Melbourne; Edward Gumersall, Atbara, Sidcup; David V. Hollingworth, Aldred House, Crescent, Salford; Alfred Holt, jun., B.A., Crofton, Aigburth, Liverpool; Clements F. V. Jackson, A.Inst.C.E., Brisbane; John Petty Leather, 17, Carlton Road, Burnley; Frank A. Lidbury, M.Sc., Owens College, Manchester; Ernest Liotard, 2, Rue de France, Nice; Thomas Stratford Logan, 52, Kirkgate, Leeds; Douglas A. MacCullum, Shawlands, Glasgow; William Mann, B.Sc., Fonnereau Villa, Dartford; John Marsh, 29, High Street, Maidstone; Joseph William Mellor, D.Sc., Owens College, Manchester; John Price Millington, B.A., Christ's College, Cambridge; John Phelps, B.A., Trinity College, Oxford; George A. P. Ross, M.B., B.Ch., 20, Westhall Gardens, Edinburgh; John William Sampson, Helpringham, Heckington; Duncan Simpson, 10, Brynmill Crescent,

Swansea; Robert Walter Sindall, 80, Manor Road, Brockley, S.E.; John Seabury Smythe, B.Sc., Ph.D., 143, Smithdown Lane, Liverpool; Walter F. Suiterst, Ph.D., Agricultural College, Holmes Chapel; George Sutherland Thomson, Government Offices, Adelaide; Henry Letheby Tidy, B.A., New College, Oxford; William Carter White, 113, Gower Street, W.C.; Lyndon Wilson, 66, Castle Gate, Newark-on-Trent.

Of the following papers, those marked * were read:—

*145. "The Specific Heats of Gases." By H. CROMPTON.

It was shown that the molecular heat of any gas at the absolute temperature T may be calculated with the help of a formula of the type $A + BT$. In this formula A has the same value for all gases, and depends on changes in the movements of the molecules of the gas as a whole. B is proportional to $V \times \log n$, where V is the volume of the molecule, and n is the number of atoms in the molecule. BT depends on interatomic changes taking place within the molecule. If for V the molecular volume at the normal boiling point of the liquid Mv_b is taken, the molecular heat at constant pressure $C_p = 4.935 + 0.000245 Mv_b T \log n$ (or if common logarithms are used the coefficient is 0.000564). The molecular heats calculated from this formula are shown to be in fair agreement with those observed. The ratio k of the two specific heats can also be calculated with the aid of this formula.

DISCUSSION.

Dr. TRAVERS remarked that it would be interesting to know how closely the formula would reproduce the values of the specific heats of the commoner gases, which had been determined with great accuracy and over a considerable range of temperature by Regnault, Witkowski, and others. The agreement between the observed and calculated values in the cases cited by the author was, however, remarkable.

Dr. PHILIP pointed out that the values of C_p given by the two formulæ (Le Chatelier's and that of the author) would, owing to the difference in the numerical constants chosen, be more divergent the lower the temperature. On this account, a study of the applicability of the proposed formula at low temperatures would be specially interesting.

Mr. CROMPTON, in reply, admitted that at low temperatures the results given by the formula did not agree with the observed so well as those obtained at higher temperatures. In explanation of this, he pointed out that the formula was only supposed to hold for an ideal gas, no account being taken of the effect on the specific heat of possible attractions between the molecules. If such attractions existed, they would have a greater influence on the specific heat at low temperatures, and this the nearer the gas was to its point of liquefaction, than under ordinary conditions. No doubt a term should be introduced to allow for the effect of molecular attractions, but at present he was unable to make any suggestion with reference to the character of this correction.

*146. "The Action of Nitric Acid on Bromophenolic Compounds." By W. ROBERTSON.

The action of nitric acid on bromophenols and their derivatives was studied in order to determine the conditions under which the bromine atom is replaceable by nitroxyl. It has been found that if the hydrogen of the hydroxyl group be replaced by either the methyl or acetyl radicle, no displacement of bromine by the nitro-group occurs when these substances are acted on by nitric acid under similar conditions. The bromohydroxybenzoic acids and their methoxy- and acetoxy-derivatives were also prepared, and it was found that with regard to them the same rule applied.

The following compounds were described:—2:6-dibromo-4-acetyl aminophenol, needles, m. p. 185–186° (Hözl. *Fourn. Prakt. Chem.*, 1886, [ii.], xxxii., 68, gives 173–174°); Friedländer and Stange, *Ber.*, 1893, xxvi., 2262, 1895°); 2-nitro 6 bromo-4-acetylaminophenol, yellow

needles melting at 230°; 2-nitro-6-bromo 4-benzoylamino-phenol, yellow needles, m. p. 247°; 2:3:6-tribromo-4-acetylaminophenol, white needles, m. p. 224° with decomposition; 2:6-dibromo-4-anisidine, white glistening leaflets, m. p. 66° (Stadel, *Annalen*, 1883, ccxvii., 70, does not give melting-point), and its acetyl and benzoyl derivatives which crystallise in needles melting at 206° and 180° respectively; acetyl-3:5-dibromosalicylic acid, m. p. 156°; acetyl-5-bromosalicylic acid, m. p. 168°; acetyl-3:5-dibromo-p-oxybenzoic acid, m. p. 207°; ethyl ester of 3:5-dibromo-p-oxybenzoic acid, needles, m. p. 99°; acetyl-3-bromo-p-oxybenzoic acid, m. p. 155°; a dibromo-m-oxybenzoic acid, m. p. 202°; 2-bromo-4:6-dinitro-3-oxybenzoic acid, a yellow substance, m. p. 217–218°.

DISCUSSION.

Mr. W. A. DAVIS pointed out that although Mr. Robertson had been unable to isolate intermediate products of nitration in the case of the bromo-phenols he had dealt with, such substances had been obtained by Armstrong and Rossiter in the form of nitro-bromo-keto-naphthalenes (*Proc.*, 1891, vii., 89). He himself had for several years been working with this class of compounds, and had found that their stability depends largely on the proportion of bromine which they contain. Thus, whilst the nitro-keto-compound of β -naphthol is so unstable that it cannot be isolated, and the keto-derivatives of bromo-, dibromo-, and tribromo- β -naphthol are stable only at low temperatures, those formed from the tetrabromo- and pentabromo-naphthols can usually be kept for several days in the dry state without undergoing change. Moreover, whilst the lower brominated keto-compounds are readily reduced to the corresponding bromonitro-naphthols by sodium sulphite, those derived from the tetrabromo- β -naphthols are reducible only by concentrated hydriodic acid.

*147. "3:5-Dichloro-o-xylene and 3:5-Dichloro-o-phthalic Acid." By A. W. CROSSLEY and H. R. LE SUEUR.

The high boiling fraction of the liquid obtained by the action of phosphorus pentachloride on dimethyldihydroresorcin consists of 3:5-dichloro-o-xylene, $C_6(CH_3)_2H_2Cl_2$, which may also be produced by the prolonged heating of dichlorodimethyldihydrobenzene with phosphorus pentachloride. It is a faintly yellow, highly refractive liquid, which boils at 129° (23 m.m.), or at 226° (atmospheric pressure), and on cooling solidifies to a mass of flaky needles melting at 3–4°.

On oxidation with nitric acid, it is converted into 3:5-dichloro-o-phthalic acid, $C_6H_2Cl_2(CO_2H)_2$, which crystallises in hair-like needles melting at 164° with previous contraction and sublimation. The anhydride (m. p. 89°) and several other derivatives have been prepared.

*148. "The Combination of Carbon Monoxide with Chlorine under the Influence of Light." By G. DYSON and A. HARDEN.

Following the method previously described (*Proc.*, 1894, x., 165), the authors have found:—

1. That when a mixture of carbon monoxide and chlorine, dried by being passed through sulphuric acid, is exposed to light, a well-marked period of photochemical induction occurs.

2. The induction lapses slowly when the exposed gas is placed in the dark.

3. The sensitiveness of this mixture to light is greatly diminished by admixture of air, but is not much affected by the presence of carbonyl chloride, hydrogen chloride, excess of carbon monoxide, vapour of carbon tetrachloride, and small amounts of water vapour.

DISCUSSION.

Professor TILDEN said one point which Dr. Harden omitted to mention was the extent to which the gases had been deprived of moisture. He would be glad to hear by what method they had been dried, and whether the authors had observed that the composition of the glass

or the condition of the surface in contact with the gases produced any influence on the rate of their combination.

Dr. HARDEN replied that the gases were dried by being bubbled through strong sulphuric acid. They had not made any experiments specially with reference to the composition of the glass or the condition of its surface.

*149. "The Constituents of Commercial Chrysarobin." By H. A. D. JOWETT, D.Sc., and C. E. POTTER, B.Sc.

Araroba, or Goa powder, and commercial chrysarobin, the substance obtained from the former by extraction with solvents as chloroform, have been investigated by Attfield, by Liebermann and Seidler, and by Hesse with varying results. The latter chemist found that crude chrysarobin contained no chrysophanic acid, but was a mixture of two parts of chrysarobin, $C_{15}H_{12}O_3$, and one of its methyl ether. He regarded chrysarobin as the anthranole of chrysophanic acid. The authors have examined commercial chrysarobin, and find that it contains the following substances, but no chrysophanic acid.

Chrysarobin, $C_{15}H_{12}O_3$, is the anthranole of chrysophanic acid and identical with chrysophanoanthrone obtained by the reduction of chrysophanic acid. It melts at 204° . When acetylated with acetic anhydride alone, a mixture or diacetylchrysarobin (m. p. 193°) and triacetylchrysarobin (m. p. 238°) is obtained, but if sodium acetate and acetic anhydride are used, the triacetyl compound is alone produced.

Methyl ether of dichrysarobin, $C_{31}H_{26}O_7$, melts at 160° . It yields a soluble pentacetyl compound, m. p. 135° , identical with Hesse's hexacetyldichrysarobin.

Dichrysarobin, $C_{30}H_{24}O_7$, does not melt below 250° , but blackens and chars gradually. On acetylation, hexacetyldichrysarobin (m. p. $179-181^\circ$) is obtained. The formula assigned to this constituent is proved by analysis.

A substance, $C_{17}H_{14}O_4$, m. p. 181° , which yields an acetyl compound, m. p. $215-216^\circ$.

The two latter substances are contained in crude chrysarobin in only small amount, the greater portion consisting of the two first named substances. Methylchrysarobin was not found to be a constituent of crude chrysarobin. Both chrysarobin and dichrysarobin yield chrysophanic acid on oxidation, and β -methylantracene by distillation with zinc dust.

Crude chrysophanic acid as obtained from rhubarb contains pure chrysophanic acid, m. p. 190° (acetyl compound, m. p. 206°), and the methyl ether of dichrysarobin, and not the methyl ether of chrysophanic acid as previously stated by Hesse.

*150. "The Constituents of an Essential Oil of Rue." By F. B. POWER and F. H. LEES.

In order to prepare some methyl nonylketone, the authors obtained a quantity of oil of rue labelled *Ol. Ruta. Ang.*, from an English distiller, and found subsequently, on inquiry, that it was not distilled from the native-grown herb. From their results, taken in conjunction with those of Thoms (*Ber. Deut. Pharm. Ges.*, 1901, x., 3), and von Soden and Hexle (*Pharm. Zeit.*, 1901, xlv., 277 and 1026), the authors regard it as most probably of Algerian origin.

The oil was light brown in colour. $d_{15.5/16} = 0.8405$, $\alpha_D = -3^\circ 48'$ for a 100 m.m. tube. It was completely soluble in two parts of 70 per cent alcohol. The following constituents were identified:—(1) Methyl *n*-heptylketone, b. p. $194.5-195.5$ at 763 m.m., $d_{14/16} = 0.8296$ (semicarbazone, m. p. $119-120^\circ$); (2) methyl *n*-nonylketone, b. p. $231.5-232.5^\circ$, $d_{20.5/16} = 0.8263$ (semicarbazone, m. p. 122°); (3) methyl *n*-heptylcarbinol, b. p. $198-200^\circ$, $d_{19/16} = 0.8273$, $\alpha_D = -3^\circ 44'$ in a 50 m.m. tube; acetate, b. p. $213-215^\circ$, $d_{20.5/16} = 0.8605$, $\alpha_D = -3^\circ 3'$ in a 50 m.m. tube (oxidation of alcohol to the corresponding ketone, b. p. $195-199^\circ$, semicarbazone, m. p. $118-119^\circ$); (4) methyl *n*-nonylcarbinol, b. p. $231-233^\circ$, $\alpha_D = -1^\circ 18'$ in a 25 m.m. tube (oxidation to corresponding ketone, oxime, m. p. $46-47^\circ$); (5) a blue oil of high but not constant boiling-point; (6) acetic acid; (7) a basic

substance having the odour of quinoline; (8) a mixture of free fatty acids; (9) methyl salicylate; (10) an ester of valeric acid, apparently ethyl valerianate; (11) pinene (nitrosochloride, nitropiperidine, m. p. $119-120^\circ$; (12) *l*-limonene (tetrabromide, m. p. 103°); (13) cineol (compound with tetraiodopyrrol, m. p. $114-115^\circ$, and hydrobromide, m. p. $55-56^\circ$).

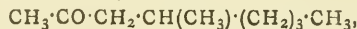
The relative proportions in which the above-mentioned substances were found to exist in the oil are approximately as follows:—The two ketones constitute 80 per cent, and were present in about equal amounts. The two alcohols represent about 10 per cent, the methyl *n*-heptylcarbinol preponderating; they were present partly in the free state and partly as acetic esters. The terpenes, together with cineol, amount to about 1 per cent, and the blue oil to about 0.5 per cent. From the non-ketonic portion of the oil, a small amount of an undistillable, viscous substance, probably a decomposition product, was separated.

Since the substances associated with the ketones and alcohols are present in such small amount, and the limonene is the more rarely occurring *l*-form, the authors conclude that all these substances are natural constituents of the oil.

*151. "Methyl β -Methylhexyl Ketone." By F. H. LEES.

Ethyl *sec*-hexylacetoacetate, $CH_3 \cdot CO \cdot CH(C_6H_{13}) \cdot CO_2Et$, was prepared by the condensation in alcohol at 100° of ethyl sodioacetoacetate with *sec*-hexyl iodide; it is a colourless oil which boils at $130-132^\circ$ (17 m.m.), and at $243-245^\circ$ under atmospheric pressure.

Methyl β -methylhexyl ketone,—



was prepared by the hydrolysis of ethyl *sec*-hexylacetoacetate with 30 per cent aqueous potassium hydroxide. It is a colourless oil with a pleasant, fruity odour, boiling at 184° (769 m.m.), and having the density $d_{15/16} = 0.8319$. Its semicarbazone forms needles and melts at 75° ; its oxime is a colourless oil.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, November 14th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

A PAPER on "The Theory of the Aluminium Anode," by W. W. TAYLOR and J. K. H. INGLIS, was read by Mr. INGLIS.

Aluminium is very slowly acted upon by dilute sulphuric acid even at moderately high temperatures. With dilute hydrochloric acid the action is violent, and it is found that if a little hydrochloric acid or soluble chloride be added to dilute sulphuric acid, the action is as violent as with hydrochloric acid of the same concentration. The object of the present paper is to find an explanation of this anomalous behaviour of sulphuric acid, and of the effect produced by the addition of chloride. It has long been known that, when an aluminium electrode is employed as anode in a solution of a sulphate or sulphuric acid, there is a very great resistance offered to the current, and that this resistance is due to a film which separates the electrode from the solution. If the aluminium is the cathode, or if other acids are substituted for sulphuric acid, this great resistance does not exist. It seems probable that the two phenomena are related, and that the film is also the cause of the slow action of sulphuric acid on aluminium. The authors have attempted to establish a theory which will explain these phenomena. The paper opens with a historical account of the subject; and it is pointed out that the question is now of practical importance in con-

nection with the use of aluminium electrodes for the conversion of alternating currents into direct currents. The first experiments were made with a cell consisting of aluminium and platinum electrodes in dilute sulphuric acid, and were carried out to ascertain in what way the addition of certain salts affected the aluminium anode. The influence of potassium chloride, bromide, nitrate, acetate, chlorate, and thiocyanate in various concentrations was investigated, and the authors conclude that the presence of certain ions enables a large current to pass through the cell. The reason seems to be that the film of aluminium hydroxide with which the anode is covered is permeable to certain ions but impermeable to others. The anomalous behaviour in sulphuric acid would then be due to the impermeability of the film to the SO_4 ions, and also to the Al^{+++} ions. This explanation is in accord with the fact that reversal of the potential-difference acting upon the cell immediately causes a current to pass, the film being permeable to H^+ ions. Experiments were next made upon the rates of diffusion of various ions through a film of aluminium hydroxide. It was found that several salts of potassium diffused rapidly through such a film, but that the sulphate passed through very slowly. This strengthens the argument that the abnormal behaviour of aluminium anodes in sulphuric acid is due to impermeability. It is suggested that the very small current which does pass may be due to a secondary action at the anode, in which the ions of water take part. The theory is confirmed by a series of experiments in which the peculiarities of the aluminium anode are reproduced by means of a platinum anode coated with a film of aluminium hydroxide. A further test was applied in the direct measurement of the resistance of a film of aluminium hydroxide to the passage of different ions. Quantitative experiments which the authors have performed on the effect of the presence of different ions on the reaction between aluminium and sulphuric acid, show that this reaction is considerably accelerated by the addition of potassium chloride.

Dr. LEHFELDT said that the lines of explanation were probably correct. Referring to the behaviour of an aluminium anode in sulphuric acid, he said that the small amount of conduction might be due to the fact that the film was not quite impermeable.

The CHAIRMAN called attention to one of the experiments described in the paper, in which a potential-difference of 50 volts applied to a cell with a membrane of aluminium hydroxide between the electrodes produced a current of 0.07 ampère, and asked what the current would have been if the voltage had been reversed.

Mr. CAMPBELL mentioned some experiments which he had seen performed with an aluminium rectifier. He said that if an alternating E.M.F. of small magnitude was applied to the electrodes of a cell consisting of two aluminium plates immersed in strong sulphuric acid, the electrostatic capacity of the cell was large, but if the E.M.F. was increased the capacity fell considerably, and then did not recover on reducing the applied E.M.F. till the cell had been allowed to rest for some considerable time. He asked for an explanation of this phenomenon.

Prof. AYRTON asked the authors whether the rectifying power of an aluminium anode was a question of resistance or of back E.M.F. He said that if an aluminium anode and a lead cathode were placed in a solution of Rochelle salt and an E.M.F. applied for about an hour, it was then impossible to send a current through the cell even by increasing the E.M.F. to 120 volts. If such a cell was used as a rectifier, a black deposit was formed on the aluminium plate which remained constant in weight. If a direct current was sent through the cell, a white deposit was formed and the aluminium plate lost in weight. Prof. Ayrton described some experiments which seemed to show that the properties of these cells were connected with changes in the liquids of the cells.

Mr. INGLIS, in reply to the Chairman, said that in the particular experiment referred to a reversal of the E.M.F. would have given a current of about 30 ampères. In the experiment mentioned by Mr. Campbell the explanation might be that when the E.M.F. was large the ions could permeate into the interstices of the film, and produce an effect corresponding to a diminution of electrostatic capacity. He thought that the power of an aluminium anode as a rectifier was due to increased resistance and not to back E.M.F.

A paper on "A Determination of the Ratio of the Specific Heats at Constant Pressure and at Constant Volume for Air and Steam" was read by Mr. MACKOWER.

The method employed in this paper is similar to that used by Lummer and Pringsheim, and consists in allowing the gas under investigation to expand adiabatically, and measuring the lowering of temperature caused by such expansion. The chief modification introduced was the substitution of a platinum thermometer with compensating leads for a bolometer strip. The electrical contacts were made by a specially constructed mercury switch, instead of by hand, and it was found possible to work with smaller quantities of gas than Lummer and Pringsheim had used. In the experiments with air the vessel used was about 50 litres capacity. The pressures were measured with an oil manometer, and the temperatures with the platinum thermometer. The time which elapsed between the instant of reducing the pressure and the reading of the final temperature was determined by means of a chronograph, and varied in the experiments described in the paper from 0.5 second to five seconds. The value of γ must be corrected on account of conduction and convection during this interval. A correction was also applied to eliminate the effect of radiation from the vessel to the thermometer. The author's value for the ratio of the two specific heats in the case of air is 1.401. In the case of steam, a cylindrical copper vessel of about 9.3 litres capacity was used. The vessel was enclosed in a copper jacket filled with steam so that the steam in the inner vessel was superheated about 10°C . The pressure in the jacket was kept constant by means of an automatic gas-regulator, devised by Prof. Callendar, which controlled the supply of coal-gas reaching the burner employed for the generation of the steam. The observations with steam were similar to those in the preceding experiments, but special precautions were necessary to prevent the condensation of the steam in the tubes leading to the vessel. The results for steam were not sufficiently accurate to justify the application of corrections for radiation, and for conduction and convection. The values of γ deduced from two series of experiments were 1.307 and 1.304.

Prof. CALLENDAR congratulated the author upon the good agreement of the results of a difficult experiment. He mentioned the difficulties in overcoming conduction when working with steam at a high temperature, and pointed out that the author's value for the ratio between the specific heats of steam agreed closely with that which he (Prof. Callendar) had recently deduced from theoretical considerations. An important feature of the present paper was that experiments had been performed in which different periods of time elapsed between the releasing of the pressure and the determination of the final temperature. Referring to the fact that the author had used a platinum thermometer instead of a bolometer strip, he said that although a bolometer strip was more sensitive than a platinum thermometer it was more sensitive than necessary in such an experiment. Another point in the experiments was the use of smaller quantities of gas than had hitherto been employed, an advantage of importance when dealing with rare gases. Prof. Callendar then exhibited and described the pressure-gauge referred to by the author and used in his experiments.

The Society then adjourned until November 28th,

ROYAL SOCIETY OF NEW SOUTH WALES.

THE General Monthly Meeting of the Society was held at the Society's House, No. 5, Elizabeth Street North, on Wednesday evening, October 8, 1902; Prof. WARREN, M.Inst.C.E., Wh.Sc., President, in the Chair.

The following papers were read:—

"Occurrence of the Mineral Gadolinite at Cooglegong, Pilbarra District, West Australia." By BERNARD F. DAVIS, B.Sc. (Communicated by Prof. DAVID, B.A., F.R.S.).

The specimen of gadolinite described in this paper was identified as such by Professor David and Mr. W. G. Woolnough, when it was brought over last year to Sydney University by Mr. Bernard F. Davis. Mr. Davis kindly undertook to make an analysis of the mineral, and place the results at the disposal of the Royal Society of New South Wales. The mineral occurs in lodes, associated with tinstone and monazite contained in gneiss. It was found by Mr. Davis at Cooglegong, in the Pilbarra District, West Australia. The following is the analysis by Mr. Davis:—

SiO ₂	..	..	..	..	23.33
FeO	..	..	..	..	10.38
BeO	..	..	..	..	12.28
Ce ₂ O ₃	..	..	..	..	2.50
La ₂ O ₃ and Di ₂ O	..	..	..	..	18.30
Y ₂ O ₃	..	..	..	..	33.40
MgO	..	..	..	..	0.69
Loss on ignition	..	..	..	..	0.32

101.20

Dr. Norman Collie examined the mineral for helium and other gases. He says that 10 grms. on heating gave about 10 c.c. of CO₂ and 10 c.c. of hydrogen, a little nitrogen, and about one bubble of helium.

"Pot Experiments to Determine the Limits of Endurance of different Farm Crops for certain Injurious Substances. Part I. Wheat." By F. B. GUTHRIE and R. HELMS.

The authors describe experiments to test the effect upon the growth of the wheat plant of the following substances occasionally found in the soil and in manures, and which are known when present in excessive quantities to act as plant poisons:—Sodium chloride and sodium carbonate, which are present in many of the artesian bore-waters used for irrigating; ammonium sulphocyanide, which has been found in impure samples of ammonium sulphate; sodium chlorate, occasionally present in sodium nitrate; and arsenious oxide, which may be present in superphosphate which has been manufactured with acid derived from sulphur or pyrites containing arsenic. The experiments were carried out in cylindrical galvanised iron culture pots of familiar construction, and were located, with the kind permission of Mr. J. H. Maiden, in the Botanic Gardens. Details of the soil and manures employed, and of the appearance at different stages of the plants treated with varying proportions of the substances under examination were supplied. The following table summarises the principal results obtained:—

Effect upon Germination and subsequent Growth of Wheat of different Percentages of Injurious Substance in the Soil.

	Germination affected.	Germination prevented.	Growth affected.	Growth prevented.
NaCl ..	0.05	0.20	0.05 to 0.15 (recovered)	0.20
N ₂ CO ₃ ..	0.30	0.5 to 1.0	0.10	0.40
NH ₄ CNS ..	0.005	0.01	0.001	0.005
NaClO ₃ ..	Above 0.01	0.05	0.001	0.003
As ₂ O ₃ ..	0.05	0.50	0.05	0.10

OBITUARY.

SIR WILLIAM ROBERTS-AUSTEN, K.C.B., F.R.S.

It is with very great regret that we announce the death of Sir William Chandler Roberts-Austen, which occurred at the Royal Mint on Saturday last, November 22nd.

Sir William Roberts-Austen was born in 1843, and was therefore fifty-nine years of age. He was of Welsh descent through his father, whose name was George Roberts, and his mother belonged to the old Kentish family of Chandler. In 1885, at the request of his uncle, the late Major Austen, J.P., of Haffenden and Cambourne in Kent, Sir William (then Mr.) Roberts obtained Royal licence to take the name of Austen.

In 1861 he entered the Royal School of Mines with the intention of becoming a mining engineer, but on obtaining the Associateship, the late Professor Graham, then Master of the Mint, secured his services. With him he carried on a long series of researches, and on Professor Graham's death in 1869, Mr. Roberts succeeded to one of the appointments that he held, viz., that of Assayer to the Mint. Thirteen years later, in 1882, he became Queen's Assay Master.

In 1880, on the retirement of the late Dr. Percy, F.R.S., he was appointed to the Chair of Metallurgy at the Royal School of Mines, where less than twenty years previously he had been a student. This appointment he held till his death, though only a few weeks ago he was compelled, through failing health, to request his great friend, Dr. Gowland, to finish the current course of lectures on his behalf.

The present writer was one of those students who attended Sir William Roberts-Austen's first course of lectures in 1880, and he remembers well the enthusiasm and energy with which the late professor entered on his work. As a teacher he was a universal favourite, and was never tired of helping and encouraging his students, both past and present. It was Sir W. Roberts-Austen who inaugurated the annual tours for his students through some metallurgical district; the first one in 1881 to Swansea and the neighbourhood is still vivid in the writer's mind; just as the train was leaving Paddington the news was received of the death of Lord Beaconsfield.

Apart from his work as Chemist to the Mint, and his Professorship at South Kensington, Sir William Roberts-Austen was well-known and esteemed in purely scientific circles. As far back as the year 1868 he wrote a paper on "The Occurrence of Organic Appearances in Colloid Silica obtained by Dialysis," which was published in the *Journal of the Chemical Society*. In the following year he published "Some Experiments illustrating the Expansion of Palladium during the Formation of its Alloy with Hydrogenium." His principal work, however, was on alloys and metallurgical subjects, with which his name will always be closely connected; his last paper, in conjunction with Dr. T. K. Rose, published in the *CHEMICAL NEWS* in 1900 (vol. lxxxi., p. 241), being on "Certain Properties of Alloys of Gold and Copper."

Sir William was elected a Fellow of the Royal Society in 1875, and has held numerous posts, all of which he filled with distinction. He was President of the Iron and Steel Institute in 1899, Hon. General Secretary to the British Association for the Advancement of Science, Vice-President of the Chemical Society, the Physical Society—of which he was also one of the founders—and of the Society of Arts. He served on the British Executive of the Paris Exhibition of 1889, and was Vice-President of the International Mining and Metallurgical Congress in Paris, receiving from the President of the Republic the Cross of Chevalier of the Legion of Honour.

In 1888 he was made a C.B., and in 1899 he was created K.C.B. He was also a D.C.L. of the University of Durham.

Among other appointments, Sir William was a member

of the Explosives Committee of the War Office, where his knowledge and experience in metallurgical matters made his opinion of great value.

Though in failing health, his death was unexpected, and he will be sincerely mourned by a large number of friends, scientific and otherwise.

NOTICES OF BOOKS.

Chemisches Praktikum. I. Teil. Analytische Übungen ("Practical Chemistry. Part I. Analytical Exercises"). By Dr. A. WOLFRUM. Leipzig: Wilhelm Engelmann. 1902.

THIS course of practical chemistry comprises both elementary and advanced technical analysis. The book is divided into three parts. The first deals with qualitative analysis of inorganic and organic substances, including under the latter heading many technical products; this section being particularly well written. Some parts of the introduction, however, might be revised with advantage; for instance, the discussion of the degree of dissociation on page 5 is distinctly misleading. The methods of detection of organic substances will certainly be found useful, being concise and in a handy form for reference. The second part of the book is devoted to quantitative analysis in all its branches, including all ordinary methods of determination. More detailed descriptions of some of the experiments would improve the book, regarded from the point of view of the student who relies on it alone for his information. The last part treats of quantitative technical analysis of various commercial products, but no food products are included. As far as possible, having regard to the necessarily restricted space devoted to this section, the accounts appear to be very complete.

Beiträge zur Chemischen Physiologie und Pathologie. ("Contributions to Chemical Physiology and Pathology"). Edited by FRANZ HOFMEISTER. Band III. 1-3 Heft. Braunschweig: Friedrich Vieweg und Sohn. 1902.

THIS recently issued number of the *Beiträge* begins the third volume. The six papers which it contains fully maintain the high standard of interest of former numbers. They include a paper by E. Friedmann describing researches aimed at determining the constitution of cystin, and enumerating the properties of some of its derivatives and another on the action of chloroform on hæmoglobin; the evidence seems to point to the fact that this action, brings about essential changes in the structure of the hæmoglobin molecule. A third paper, by Fr. N. Schulz and R. Zsigmondy, gives the result of investigations of the "gold number" of various albuminous substances. Apparently this number, of which the definition according to Zsigmondy is given, may, like other physical and chemical properties, such as optical activity and temperature of coagulation, be regarded as a definite means of distinguishing albumens.

Merck's Index. Second Edition. Darmstadt: Eduard Roether. 1902. Pp. 374.

THE first edition of this book, published five years ago, being exhausted, it has been found advisable to issue a second. The same plan has been adhered to as was adopted for the first edition, but its scope naturally has been much enlarged, and a good deal of attention has been devoted to the needs of physicians and pharmacists.

The name of "Merck" in connection with this subject is very widely known, and the firm is constantly bringing forward new drugs derived from the never-failing coal-tar

products; we must, however, urge that great caution be exercised in their use, especially at first. What is one man's meat is another man's poison, and the same can be truly applied to many of these new preparations. Prolonged and careful experiments are necessary before many of these bodies should enter into general use.

The book is divided into six parts. The first comprises chemical bodies and definite principles, certain galenical preparations and organic extracts; the second, special solutions and forms of substances used in analytical and microscopical work; the third, crude drugs; the fourth, minerals; the fifth, collections suitable for schools and museums; and the sixth, sundries.

A noticeable feature in this new edition is the information on the chemical and physical properties of the substances included, and also that on the technical application of various bodies.

The Painters' Laboratory Guide, and Handbook on Paints, Colours, and Varnishes for Students. By GEORGE H. HURST, F.C.S., &c. With 22 Illustrations. London: Charles Griffin and Co., Ltd. 1902. Pp. 248.

IF the author had called this book the "Paint Makers'" laboratory guide he would have expressed the character of the work better than is done by the present title. In his opening sentences he shows that it is with paints on the large scale that we have to deal, and these paints may be described as fulfilling two objects, viz., protection and decoration.

The book is divided into ten chapters, of which five (Chapters II. to VI.) deal with the preparation of pigment colours. As a general rule the author first describes the pigment, whether a natural or artificial product; if the former, the localities whence it is obtained are mentioned; if the latter, the processes of manufacture are described, with instructions for carrying them out on a small scale in the laboratory when possible. Chapter VII. is on "Lakes," and here the author has given special attention to their preparation from coal-tar dyes owing to the rapidly increasing importance of these bodies. The class of pigments known by the name of lakes is possessed of special properties that serve to distinguish them from purely mineral pigments; they owe their colour to organic colouring matters and dye-stuffs, and in more recent years the use of the coal-tar dyes has been pressed into service to replace the natural products, such as cochineal, logwood, &c.; still it is essential that a metallic oxide be present in their preparation, and it is this oxide entering into combination with the acid principle of the organic matter used that forms the basis of lake making. In this section the author has introduced a simplification in the manner of writing the names of the coal-tar derivatives; instead of running a dozen syllables or more all together, as is unfortunately the present custom; he sub-divides the word into its natural components by means of hyphens, thus:—Para-nitro-benzene-azo-beta-naphthol instead of paranitrobenzeneazobetanaphthol; there can be no question as to which is the more easily read and quickly understood, and though we are afraid it is asking a great deal, we should be very glad to see the change made generally.

There is no legitimate reason why what is really a short descriptive sentence should be printed and written as if it were simply one word, and when sub-divided, as the author has done in this volume, the names of the organic products are both easier and quicker to read. So much work in organic chemistry has been done in Germany, that chemists have unfortunately adopted the German style of combining all the descriptive adjectives into one word, "portmanteau" words Mark Twain called them; but the method is clumsy and quite as un-English as if we were to write down a certain steam-engine as a fifteen thousand horsepower reciprocating triple expansion-condensing marine steam engine, or to write of extra

superfinecream laid blue ruled white foolscap writing paper, for example.

Chapters VIII., IX., and X. are on "Paint-oils and Thinners," "Driers," and "Varnishes," respectively, and form an important section, while the book closes with a good index of seven pages of double columns.

CORRESPONDENCE.

"FIXING" NITROGEN FROM THE ATMOSPHERE.

To the Editor of the Chemical News.

SIR,—The combination of atmospheric oxygen and nitrogen by electric arc, with formation of nitric acid or nitrate, as sketched in the CHEMICAL NEWS (lxxxvi., p. 238) and elsewhere, will have the interesting consequences of diminishing the total weight of the atmosphere as well as of impoverishing the remaining atmosphere in oxygen. Oxides of nitrogen are formed, absorbed by water or alkali to nitrates and nitrites. That is, NO_2 is formed (subsequent conversion to all nitrate by atmospheric oxygen would mean $\text{N}_2:\text{O}_5$), containing about 70 per cent by weight of oxygen, from air containing about 23 per cent by weight of oxygen.

In all fuel and other combustion the oxygen of the atmosphere is diminished; in this combustion of atmospheric nitrogen, the nitrogen as well as the oxygen is for the time being taken out of the atmosphere, and in undesirable ratio.

The weight of remaining atmosphere will be very large indeed, but an annual 12 million tons of nitrate of soda would be a serious additional draft on the oxygen of the atmosphere. The increase of green leaf surface would not be more than proportional to increase of population.—I am, &c.,

W. H. DEERING.

Woolwich, November 17, 1902.

ANALYSIS OF APATITE.

To the Editor of the Chemical News.

SIR,—The following is the analysis of some crystals of apatite that were obtained near Antwerp, Jefferson County, New York, some time ago. They were olive-green prisms, and were about 2 c.m. long and 8 m.m. in diameter. The analysis was made in the Chemical Laboratory of Cornell College by Assistant Frank L. Hann.

	Per cent.
P_2O_5	41.0
CaO	48.2
$\text{Ca}_3(\text{PO}_4)_2$	89.2
SiO_2	0.6
Al_2O_3	9.0
CaF_2	1.2
	100.0

—I am, &c.,

NICHOLAS KNIGBT.

Mount Vernon, Iowa,
November 4, 1902.

Action of Isocyanate of Phenyl on the Ethers of some Oxy-acids.—E. Lambling.—In a long paper the author describes a number of experiments on the action of isocyanate of phenyl on the ethers of glycolic, lactic, and phenylglycolic acids, and he describes, for each of these acids, the phenylurethane of the ether, that of the corresponding acid and the lactame derived from this acid.—*Bull. de la Soc. Chim. de Paris*, xxvii., No. 10.

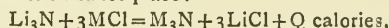
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

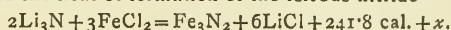
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 18, November 3, 1902.

Aluminium Chlorosulphate.—A. Recoura.—By crystallisation of a solution of aluminium sulphate in boiling hydrochloric acid the author obtains the chlorosulphate of aluminium, $\text{AlSO}_4\text{Cl} \cdot 6\text{H}_2\text{O}$. This substance is very soluble in water and very slightly soluble in alcohol. Cryoscopic measurements show that the solution in water is, not even at first, anything more than a simple mixture of aluminium sulphate and chloride. The lowering of the freezing-point of the aqueous solution of this compound is the sum of the respective lowerings of the sulphate and the chloride. The various experiments performed on this salt lead the author to believe that it has the same constitution as chromium chlorosulphate.

A General Method of Preparing Metallic Nitrides.—M. Guntz.—The author in a previous research measured the heat of formation of lithium nitride. If this substance is allowed to react on a metallic chloride, MCl , the following reaction takes place:—



and the number Q is generally very considerable, because lithium chloride is one of the chlorides formed with the largest evolution of heat. Thus, in the following reaction if x is the heat of formation of the ferrous nitride—

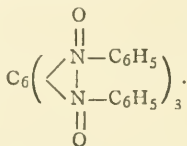


There is a considerable excess of heat in this case, allowing for the formation of the ferrous nitride. The author, therefore, uses such a reaction to prepare the nitrides of iron, Fe_3N_2 and FeN . Li_3N acts on FeCl_3KCl in a very energetic manner. The two products should first be pulverised, and then gently mixed in a crucible. This is heated, and after cooling the contents washed with boiling water and then dried at 100° . The nitride thus obtained, FeN , is a black compound which when heated on platinum foil becomes incandescent and is transformed into iron oxide.

Barium-ammonium and Barium-amide.—M. Mentrel.—It has already been shown that metallic barium and strontium dissolve in liquid ammonia to give definite compounds. The author now examines the conditions of formation of barium-ammonium and its properties. His method of preparation consists in passing ammonia gas over barium. The metal is not attacked above $+28^\circ\text{C}$. Below this temperature a red solid product is obtained which is transformed into a blue liquid when the temperature sinks below -23° . Towards -50° an oily dark blue liquid separates, slightly soluble in liquid ammonia, colouring it blue. Below -23° these compounds are stable; at -15° they are transformed into the amide, and this transformation takes place more rapidly as the temperature is raised. An analysis of the various products gives:—At 0° , $\text{Ba} + 6.1\text{NH}_3$; at -23° , $\text{Ba} + 6.3\text{NH}_3$; and at -50° , $\text{Ba} + 6.97\text{NH}_3$. At low temperatures, therefore, the barium-ammonium contains ammonia in slight excess, proving the solution of this gas in the solid compound. The formula of the latter apparently is $\text{Ba}(\text{NH}_3)_6$.

Some Oxidation Products of Aniline.—C. I. Istrati.—The air has a considerable action on aniline at its boiling-point. At the same time as it unites with oxygen condensation takes place. During the reaction a quantity of water is produced, and a little ammonia. After ten hours of boiling, the aniline becomes brown; after ten days, it is brown and viscous. Gradually it deposits blackish crystals, and the mass becomes completely solidified by about the twenty-fifth day. This mass is filtered and washed with cold alcohol. A brownish red substance remains on the filter and a black liquid passes

through; this latter containing all the non-oxidised aniline. Chloroform dissolves out from the former substance a dark red material, having apparently the formula $(C_6H_5-NH)_3\equiv C_6H_2-O-C_6H_2\equiv(NH-C_6H_5)_3$. The portion insoluble in chloroform, on purification, yields long colourless crystals melting at $238-239^\circ$, and apparently of the formula—



Estimation of Carbon Monoxide and Carbon Dioxide in Vitiated Air.—Ferdinand Jean.—The author devises a simple and practical apparatus by which the amount of carbon monoxide and carbon dioxide in confined spaces may be rapidly estimated.

MISCELLANEOUS.

Phosphates of Rubidium and Cæsium.—Ed. von Berg.—These substances are obtained by saturating PO_4H_3 by the bases or their carbonates. *Monorubidic phosphate*, PO_4RbH_2 , is obtained from its solution in beautiful quadratic prisms, by concentrating first by heat and then in the desiccator; it has an acid reaction, is very soluble in water, but insoluble in alcohol. *Dirubidic phosphate*, $PO_4Rb_2H + H_2O$, is very difficultly crystallisable in indistinct grains, very soluble in water, insoluble in alcohol, and has an alkaline reaction. This salt was obtained by leaving the product obtained by the addition of concentrated ammonia to its solution, in the desiccator over sulphuric acid; a slightly soluble white precipitate is formed of a double phosphate which gradually loses its ammonia in the desiccator. *Trirubidic phosphate*, $PO_4Rb_3 + 4H_2O$, occurs in badly formed prisms and is very hygroscopic. *Metaphosphate of rubidium*, PO_3Rb , is obtained by the calcination of the monorubidic salt as a white powder, absolutely infusible, very soluble, and with a neutral reaction. *Pyrophosphate of rubidium*, $P_2O_7Rb_4$, is the result of the calcination of the dirubidic salt; it appears as a white fused mass, and has a neutral reaction. *Monocæsic phosphate*, PO_4CsH_2 , in beautiful tabular crystals, is obtained in the same manner as the rubidium salt. *Dicæsic phosphate*, $PO_4Cs_2H + H_2O$, occurs in white microcrystalline masses, and is very soluble. *Tricæsic phosphate*, $PO_4Cs_3 + 5H_2O$, resembles the last salt. *Metaphosphate of cæsium*, PO_3Cs , is a white mass, coarsely granular, very difficult to fuse, soluble in water, and has a neutral reaction. *Pyrophosphate of cæsium*, $P_2O_7Cs_4$, forms a colourless glass; it is very deliquescent, and has an alkaline reaction.—*Berichte*, vol. xxxiv., p. 4181.

The Acetylacetic Compounds of Platinum.—A. Werner.—For the sake of convenience the term acetylacetone will be represented in this note by the formula AcH . A boiling solution of chloroplatinate of potassium being treated with KOH , not in excess, and shaken up with AcH , soon becomes cloudy, and deposits orange coloured crystals; then after a few hours, further crystals of a bright yellow colour. The former are fairly soluble in water, but insoluble in the organic solvents, slightly soluble in water containing KOH or KCl , and give no colouration with Fe_2Cl_6 . Their composition is $PtClAc.KCl$. The yellow salt is distinguished from the preceding one, in that its aqueous solution gives a yellow precipitate with hydrochloric acid, and this amorphous precipitate is only slightly soluble in water, but soluble in the organic solvents. The formula of the yellow soluble salt is $PtAc_2.KCl$, and the yellow precipitate formed by hydrochloric acid is the acid correspondent $PtAc_2.HCl$. The corresponding rubidium salt is soluble in water, and crystallises in alcohol in long yellow needles. A pre-

paration analogous to the one described above, but with an excess of potash, still gives a yellow crystalline precipitate, but of a more simple composition; this is a platinous acetylacetone, $PtAc_2$. It can be crystallised in benzene in beautiful yellow crystals, and is not decomposed by strong acids. Finally, if we operate in an analogous manner on chloroplatinate of potassium with AcH and a strong solution of soda, we observe first that golden-yellow crystals are deposited, followed by a second lot of less soluble greenish yellow crystals. The first salt is soluble in water, and less soluble in the presence of alkalis; the solution is coloured deep red by Fe_2Cl_6 , and gives precipitates with the metallic salts. This salt is $PtAc_2.2NaCl + 5H_2O$. If we boil its aqueous solution it changes to a brown colour; if we stop this action before it becomes black and add $NaCl$, we obtain a deposit formed of a yellow salt contaminated with resinous products. On taking up with chloroform, we obtain beautiful yellow crystals, very soluble in water; this salt is $PtAc_2.NaCl + 2H_2O + CH_3Cl$. The aqueous solution, treated with hydrochloric acid, gives a precipitate of $PtAc_2.HCl$.—*Berichte*, vol. xxxiv., p. 2584.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 1st.—Society of Arts, 8. (Cantor Lectures). "The Future of Coal-gas and Allied Illuminants," by Prof. Vivian B. Lewes.

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Royal Institution, 5. General Monthly Meeting. Society of Chemical Industry, 8. "The Influence of Impurities on the Specific Gravity of Sulphuric Acid" and a "Note on the Determination of the Strength of Sulphuric Acid," by Arthur Marshall, F.I.C., F.C.S. "The Interaction of Sulphurous and Nitrous Acids as affecting various Absorbents Employed in Testing the Gases escaping from Vitriol Chambers," by R. Forbes Carpenter, F.I.C., &c., and J. E., Linder, B.Sc., &c.

WEDNESDAY, 3rd.—Society of Arts, 8. "Some Aspects of Photographic Development," by Alfred Watkins.

THURSDAY, 4th.—Chemical, 8. "The Absorption Spectra of Metallic Nitrates" (Part II.), by W. N. Hartley. "The Specific Heats of Liquids," by H. Crompton. "Studies in the Camphor Series—Part X, The Constitution of Enolic Benzoylcamphor" and "Note on the isomeric Benzoyl Derivatives from Isonitrosocamphor," by M. O. Forster. "The Constitution of the Products of Nitration of Meta-acetoluidide," by J. B. Cohen and H. D. Dakin.

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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2245.

CRYSTALLISED PEROXIDE OF HYDROGEN.

By WILHELM STÄDEL.

THE firm of E. Merck, of Darmstadt, has been supplying a solution of peroxide of hydrogen at 30 per cent for some years past; this peroxide fulfils all our requirements as regards purity and stability. This preparation is appreciated as an antiseptic, more especially in connection with surgical instruments and appliances. They have been able to manufacture also a sufficiently concentrated solution on a large scale. The author of this article is indebted to the courtesy of this firm for large quantities of the latter product for the purposes of research.

This research is not yet completed, but it is possible, nevertheless, to announce one fact chosen from among the most interesting ones observed, viz., that peroxide of hydrogen, contrary to recent assertions, crystallises with ease, and in a very distinct manner. Its melting-point appears to be about -2° , but it may be possibly a little higher. The preparation used contained from 95 to 96 per cent of H_2O_2 . In a freezing mixture at -20° it remained liquid; in a mixture of ether and solid carbonic anhydride it solidified into a hard resisting mass. Further, this phenomenon also occurred in chloride of methyl. The eutectic point thus appears to be between -20° and -23° . If we throw a trace of the solid peroxide into the liquid cooled down to -8° or -10° , there immediately form magnificent needle-shaped crystals, as transparent as water, and which soon permeate the whole mass. By draining the mother-liquor from the crystals and allowing these to regain their liquid state by fusion, we can obtain, by means of a second crystallisation, peroxide of hydrogen free from water.

Repeated analyses have given the composition of these crystals as 100 per cent H_2O_2 . Similar crystals can be obtained from more dilute solutions titrating 90 or even 80 per cent of H_2O_2 . It seems that practically we may look upon it as possible to prepare a pure peroxide of hydrogen without having recourse to an operation, which is not always free from danger; that is to say, to the distillation of high percentage solutions, as done by Wolfenstein and Brühl, or Spring, to obtain anhydrous peroxide of hydrogen.

For the better manifestation of the most marked properties of peroxide of hydrogen, a series of experiments was devised. Thus, an extremely small quantity of platinum black produced a catalytic decomposition accompanied by a violent explosion; powdered binoxide of manganese, or a mixture of carbon and powdered magnesium with a trace of binoxide of manganese, takes fire immediately when put in contact with anhydrous peroxide of hydrogen, or thrown into its solution at 90—95 per cent. Finely divided iron (reduced iron) alone is without action; the liquid simply mixes with the powder, but if we add now a little binoxide of manganese a flame is produced, and the iron burns, throwing off sparks. Powdered lead becomes enflamed in the same manner. A few drops of anhydrous peroxide of hydrogen thrown on to wool or a moist sponge immediately bursts into flame.

Monohydrated sulphuric acid can be mixed with anhydrous peroxide of hydrogen if it is done at a low temperature.

The refrigeration must be sufficient to counteract the evolution of heat which takes place. If the operation is not conducted under these conditions, oxygen very rich in ozone is given off. The examination of this reaction is not yet complete; it may be possible to produce persulphuric acid by these means.

We can also make use of peroxide of hydrogen in two reactions. The most interesting one, that is to say, that of which the best use can be made, takes place with sulphate of titanium. By its help we are able to detect 1 part of peroxide of hydrogen in solution in 1,800,000 parts of water. When the ratio is only 1:18,000 the reaction is manifested by the appearance of a deep yellow colouration, becoming bright yellow for 1 in 180,000, and remaining yellowish in a fairly thick layer with 1 part in 1,800,000. The action on ceric sulphate and ammonia is less sensitive; it reaches its limit of sensitiveness when the solution is diluted to 1 in 180,000. It must also be remarked that if the solutions in which we have produced the titanium reaction are still coloured after several days, this cannot be said of the cerium solutions, which in a very few days become completely colourless.

We know that peroxide of hydrogen is capable of forming crystallised compounds with metallic salts. M. Tanatar has described some of these bodies. The compound containing cadmium lends itself very well to the demonstration. On pouring a 90—95 per cent solution of peroxide of hydrogen into a concentrated solution of chloride of cadmium the mass becomes thickened by the formation of small, fine, white silky flakes. When collected and dried it has been found that they contained about 23 per cent of peroxide of hydrogen.

It may be concluded from the above that the problem of the preparation of anhydrous peroxide of hydrogen on the large scale has been solved. The economic results of this achievement will be known to us in the future. But from the point of view of facts already known, we may say with safety, that the use in surgery of an antiseptic product incapable of introducing foreign matters into wounds, or of producing anything besides water and oxygen by its decomposition, is made practicable by the present preparation; we are perfectly justified in hoping for great results in this direction.

In conclusion, we may remark that anhydrous peroxide of hydrogen, prepared by means of crystallisation, appears to be easily transported. A well-packed sample was placed on a truck and set on a journey of 50 or 60 kilometres, without undergoing any change. A second sample was treated in the same manner for three days without experiencing any injury.—*Zeitschrift für Angewandte Chemie.*, 1902, p. 642.

LABORATORY NOTES.

By HORACE JERVIS.

Eliminating Ammonium Salts.—Ammonium salts accumulated during the course of mineral analyses may be driven off (prior to the estimation of small amounts of magnesia say) either by direct vaporisation or by heating with nitric acid. The latter procedure is considered the more elegant; but the former need not be the spluttering, tedious, and generally unsatisfactory operation it is oft represented to be. It goes very smoothly if, after evaporating the liquid to crystallisation of the salts in the porcelain basin, the mass is scraped into a platinum dish and the transfer then cleanly completed by wiping with a piece of ashless filter-paper. A cover of ashless paper is then pressed on to the surface of the semi solid mass. This prevents spitting and also enables the moisture to be easily driven off if the mouth of the dish is inclined towards a hot muffle. The paper so charred remains intact nearly to the end.

Self-hard Alloys.—The exigencies of modern steel-works require analyses to be made so quickly that a stream of work of a stereotyped kind is passing continually through each operator's hands. Anything unusual interrupts the rate of progress and is considered more or less a nuisance. This unphilosophic attitude of mind is not commendable, but it can hardly be avoided; it is a

difficult matter to be an artist under such conditions as a respectable artisan would find intolerable. Being so long accustomed to see work disappear at express rate by a mere turn of the wheel, as it were, such an operator hardly knows what to do with a refractory sample. He concludes that it is insoluble or incompletely decomposed if the reagents used do not make short work of it while you wait, and so we are growing accustomed to unusual mixtures of acids which affect a speedy dissolution of the sample, but are not without disadvantages; for example—

The decomposition of the ferro-alloys used for making the more modern self-hard steels (which contain 10 to 12 per cent chromium and about three times as much tungsten) are vigorously attacked by a mixture of nitric and hydrofluoric acid, and the resulting solution can be used for the estimation of tungsten and (with limitations) chromium, phosphorus, and manganese; but it cannot be used for the estimation of sulphur or silicon, and platinum wire is essential. Such alloys are incompletely decomposed when digested for an hour or two with aqua-regia. But on prolonged digestion the dark coloured insoluble residue becomes quite yellow. As several days are generally available for the complete analysis the following scheme is practicable.

Pour 10 c.c. nitric acid (1.42) and 25 c.c. hydrochloric acid over 2½ grms. of the alloy which has been crushed to pass a 90 sieve, and allow to digest in a covered beaker at a temperature well below boiling point, so that the liquid may be hardly evaporated. In two or three days, or less if the operation is kept going through the night, the sample is decomposed and may be evaporated, &c., as usual, and the residue used for the determination of tungsten and silicon and the filtrate for sulphur, phosphorus, chromium, and manganese. For the estimation of the two latter elements, however, a sodium peroxide fusion, which, on extruding, leaves all the chromium in the filtrate and the manganese in the residue, is to be preferred.

The amount of impurity (ferric and chromic oxides) associated with the tungstic oxide may be about 1 per cent of its weight. This was so in an assay just made of a typical alloy; but two or three times this amount would probably be found, if the assay was evaporated and strongly baked, as is customary when sulphur and phosphorus is being estimated.

LACTATES OF MERCURY.

By MARCEL GUERBET.

LACTATES of mercury have been investigated already by Engelhardt and Maddrel (*Lieb. Ann.*, 1847, vol. lxi., p. 95) and by Brüning (*Ibid.*, 1857, vol. civ., p. 194).

The two former writers described a mercurous lactate insoluble in water, which corresponded to the formula $(C_3H_5O_3)_2Hg_2 + 2H_2O$, and a basic mercuric lactate, soluble in water, of which the formula should be $(C_3H_5O_3)_2Hg.HgO$.

Brüning, following the directions given by the preceding writers for the preparation of this latter salt, obtained, like them, a lactate soluble in water; he believed he had identified it as a mercurous salt, and gave it the formula $(C_3H_5O_3)_2Hg_2$.

In face of these contradictions, I took up the examination of the lactates of mercury, and I am about to prove that neither the basic mercuric lactate of Engelhardt and Maddrel, nor the mercurous lactate of Brüning are definite compounds; they are mixtures of Engelhardt and Maddrel's mercurous lactate and of the mercuric lactate which I have succeeded in isolating in a state of purity, and of which I will describe the preparation.

Mercurous Lactate.—Engelhardt and Maddrel obtained this body by mixing a very concentrated hot solution of lactate of soda with a saturated solution of mercurous

nitrate. It is deposited on cooling in the form of rose-coloured crystals.

The colour of this salt is due to an impurity, for I have sometimes succeeded in obtaining it completely white; I may add that when dried at the ordinary temperature it contains only one molecule of water of crystallisation, and agrees with the formula $(C_3H_5O_3)_2Hg_2 + H_2O$.

To prepare this body, I boiled some lactic acid diluted with ten times its volume of water; in this manner the anhydrides (dilaetic acid and laetide), which are always present in the concentrated acid, are destroyed (Vislicenus, *Lieb. Ann.*, vol. clxiv., p. 181).

On the other hand, we prepare some mercurous oxide by pouring a cold solution of mercurous nitrate into a cold solution of potash in excess, and rapidly washing the precipitate in the dark; we then add the amount of dilute lactic acid necessary for the solution of the mercuric oxide, which takes place immediately. The solution is then evaporated at the ordinary temperature over sulphuric acid.

The salt is deposited on the sides of the glass in crystalline crusts formed of short, colourless, prismatic needles.

The estimation of the mercury in the form of mercurous chloride gave 67.02 per cent of the salt used. The formula $(C_3H_5O_3)_2Hg_2 + H_2O$ requires 67.11 per cent. Engelhardt and Maddrel found 64.86 per cent of mercury in their rose-coloured salt; it was estimated in the dry way, which, as we know, generally gives rather low results. They gave the salt the formula $(C_3H_5O_3)_2Hg_2 + 2H_2O$, which corresponds with 65.14 per cent of mercury.

The salt cannot be estimated directly in this salt, as it is decomposed by heat.

Mercurous lactate is not completely soluble in water; it becomes disaggregated, one part dissolves, and the other part separates as a white powder which gradually becomes grey in appearance. If the mixture is heated it becomes black, and mercury is precipitated. The portion soluble in cold water consists principally of mercurous lactate with a little mercuric lactate. As the salt is completely soluble in water containing lactic acid, it is probable that the effect of water alone is, first to dissociate it into lactic acid, by which means a portion is dissolved, and into a more basic insoluble lactate; then there follows the decomposition of the insoluble portion into mercuric lactate and mercury, which gives it the grey appearance.

Mercuric Lactate. $(C_3H_5O_3)_2Hg$.—Engelhardt and Maddrel's basic mercuric lactate is not a definite compound, as I will show later on. I was able, however, to obtain a perfectly definite mercuric lactate in the following manner:—

Lactic acid diluted with ten times its volume of water, and boiled for half-an-hour to get rid of the anhydrides it contains, is treated with an excess of recently prepared yellow oxide of mercury. Solution takes place immediately, and it can be filtered at once. The solution is then evaporated over sulphuric acid at the ordinary temperature, and the salt gradually crystallises out. In spite of all precautions taken in the preparation of the yellow oxide, and in the saturation of the lactic acid, which should be effected without allowing any disengagement of heat, there is always a small quantity of mercurous lactate formed, which remains in the mother-liquors. To obtain a mercuric lactate entirely free from this latter substance, it is necessary to wash the crystals with a few drops of water. They are then dried at the ordinary temperature.

Analysis.—1.415 grms. of the salt dried over sulphuric acid, dissolved in water and reduced by phosphorous acid in the presence of hydrochloric acid, gave 0.880 gm. of mercurous chloride, which corresponds to 52.82 per cent of mercury. The formula $(C_3H_5O_3)_2Hg$ requires 52.91 per cent.

Properties.—Mercuric lactate is deposited from its aqueous solutions in the form of colourless, prismatic needles grouped together in bundles.

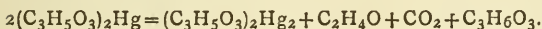
It is very soluble in water; 1 part of water at 20° dissolves 2.75 parts of the salt. Under the influence of heat the solution undergoes a curious decomposition.

If it is boiled there is no appearance of any transformation, but in reality the mercuric salt gradually changes to the mercurous salt; for the solution which at first gave no precipitate on the addition of hydrochloric acid, gives a precipitate of mercurous chloride if the reagent is added after a few seconds' boiling.

At the same time, carbonic acid is formed; this can be recognised by means of lime-water, and also ordinary aldehyde, recognised by its odour. The latter can also be detected by distilling a few drops of the liquid, which reduces an ammoniacal solution of nitrate of silver, colours red fuchsin which has been decolourised by sulphurous acid, and precipitates acetate of phenylhydrazine.

Further, at the same time, lactic acid is set free. It is observed that the boiled solution, treated with a drop of potash, gives a precipitate of oxide of mercury, disappearing on agitation, while the original liquid leaves a permanent precipitate of this oxide on the addition of a trace of potash.

The transformation effected by boiling takes place according to the formula:—



Now that we know the properties of the lactates of mercury, let us return to the lactates prepared by Engelhardt and Maddrel, and by Brüning.

The first of these salts should have the formula $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Hg} \cdot \text{HgO}$. The authors obtained it by saturating a dilute boiling solution of lactic acid with red oxide of mercury, filtering, concentrating to a syrupy consistence, and allowing it to crystallise. First of all, yellow crystals insoluble in water were deposited, then very soluble, colourless crystals. On taking up with boiling water, filtering and evaporating over again, brilliant prismatic crystals were obtained, grouped round a centre; they were very efflorescent and easily soluble in both hot and cold water.

Brüning, following the above instructions, obtained, like Engelhardt and Maddrel, a salt soluble in water, and undecomposed by boiling water. Its solution, treated with hydrochloric acid, allowed the whole of the mercury present to be precipitated in the form of mercurous chloride; further, he gave it the formula of a mercurous lactate, $(\text{C}_3\text{H}_5\text{O}_3)_2\text{Hg}_2$.

These different chemists, working under the same conditions, thus obtained, the two former a *mercuric lactate*, the latter a *mercurous lactate*.

In face of this disagreement, I repeated their experiments, and following their instructions exactly, I vainly endeavoured to obtain a soluble lactate of mercury of a definite composition. I could only obtain various mixtures of Engelhardt and Maddrel's mercurous lactate, and the mercuric lactate of which I have already described the preparation. When these mixtures of the salts are rich in mercuric lactate they are soluble in water; on the other hand, they are only slightly soluble and dissociable when they are rich in mercurous lactate.

The following are the facts I have observed:—

When dilute lactic acid is boiled with red oxide of mercury, aldehyde is given off, as already observed by Brüning, and by passing the gas given off through lime-water we observe that carbonic acid is also evolved.

The solution, filtered and evaporated to a syrupy consistence, deposits the yellow crystals noticed by Engelhardt and Maddrel.

If we take up with boiling water, filter, and evaporate again, crystals are deposited which answer to the description given by these chemists, except concerning their solubility in water.

The crystals I obtained from this second crystallisation do not dissolve entirely in cold water; they leave a residue of a white powder, becoming grey and then black

when heated. Here we recognise the properties of mercurous lactate.

But these crystals also contain mercuric lactate, as their solution in water containing lactic acid and precipitated by hydrochloric acid, gives a fresh precipitate of mercurous chloride if we add phosphorous acid.

If we estimate the mercury, we find that the salt contains a minimum 65.07 per cent of mercury, with an additional 2.27 per cent for the maximum, or a total of 67.34 per cent. Engelhardt and Maddrel found 67.62 per cent. The mother-liquor, evaporated at the ordinary temperature over sulphuric acid, gave further crystals containing 58.2 per cent of mercury, of which 26.2 was the minimum and 32.0 the maximum. The second mother-liquor gave more crystals, still richer in mercuric lactate (mercury at the minimum 48.3 per cent, at maximum 7.3 per cent).

These two last mixtures of lactates are soluble in water. We might perhaps succeed in preparing by fractional crystallisation a mercuric lactate entirely free from mercurous lactate; but the operation would not be very successful as the returns would be excessively small.

However, these experiments show that the lactates, prepared by boiling dilute lactic acid with oxide of mercury, are not definite compounds, but mixtures.—*Bull. Soc. Chim.*, Series 3, vol. xxvii, No. 15.

THE MEASUREMENT OF TEMPERATURE BY ELECTRICAL MEANS.

ACCURACY of measurement in all scientific and commercial work, whether chemical, electrical, physical, or what not, is of the utmost importance.

Balances, micrometers, telescopes, &c., have all been brought to a very high pitch of perfection, but the measurement of temperatures, except within rather narrow limits, bounded on one side by the boiling-point of mercury, has been, until quite recently, very largely a matter of guesswork and conjecture.

In metallurgical and all furnace work, for instance, the question of temperature has depended upon the eye of the most experienced workman, and when this particular individual left, the whole process under his control ran the risk of being completely upset until another man acquired the necessary experience.

In many processes, such as annealing, it is important that the temperature should be known within two or three degrees. In an article on "Riddles Wrought in Iron and Steel," Mr. P. Kreuzpointer (*Cassier's Magazine*, 1901, pp. 276—280) says:—"We are comprehending that iron and steel are not the rigid immovable mass that we were wont to consider these metals; that they are, in fact, like very sensitive creatures, liable to be influenced by changes of temperature, unwilling to be abused and ill-treated. It is the degree of this changeability of steel which today requires our closest attention and study; the condition under which it changes, the reason why it changes, and what changes make a given grade of steel suitable or unsuitable for a given purpose. . . . We must use the pyrometer more freely than we do now in order to be able to determine the proper temperature at which to anneal and to temper, and to produce the same results uniformly at all times."

For many years the Cambridge Scientific Instrument Company have been experimenting with the electrical thermometers devised by Professor H. L. Callendar and Dr. E. H. Griffiths, in order to render them capable of standing the rough treatment of commercial work, and without sacrificing their well-known scientific accuracy, and they have now produced thermometers which fulfil these requirements.

The electrical thermometers made by this firm are of two kinds:—

I. *Resistance thermometers*, depending on the way in

which the resistance of a coil of wire is affected by its temperature.

II. *Thermo-electrical thermometers*, depending for their indications on the current generated by heating one of a pair of metallic junctions.

In the resistance thermometers, a fine platinum wire is wound on a mica frame; this wire is connected by means of stouter wires to the indicator or recorder. The platinum coil is protected from the action of fumes and from mechanical damage by means of a brass, steel, nickel, or porcelain tube, depending on the temperature it is required to measure. The thermometers can be placed in positions where it would be absolutely impossible to use or read mercury ones, and by means of compensating leads the indicators, where the temperature is read, can be placed at a considerable distance away, and by means of a switch-board any number of furnaces can be connected with the indicator, situated, say, in the manager's office. Again, by means of a Callendar recorder, a continuous record of the temperature can be obtained on a sheet of ruled paper.

Thermo-electrical thermometers are largely employed on the Continent for smelting, distilling, foundry-work, &c.; they will measure any temperature up to 1600° C. The couple consists of a platinum, platinum-iridium junction enclosed in a porcelain tube, and the temperature obtained is read on a special form of voltmeter, each division on the dial being equal to 10° C.; these thermometers, though not so accurate as the resistance ones, are useful for employment in places where there is a great risk of the destruction of the thermometers, their cost being less than that of the resistance ones, but as they require more frequent standardising they are not so trustworthy as resistance thermometers.

Both the above forms can be used for very wide ranges, or can be made for special purposes; they are suitable alike for cold storage rooms, for vats, stills, furnaces, &c., and if care be taken, it may be stated as a general rule that the temperature measurements can be relied upon to 0.5 per cent.

Among the advantages possessed by these instruments we may mention briefly the following:—They can be used for the measurement of very high or very low temperatures, beyond the range of the mercury thermometer; they can be placed in positions where it is impossible to use other kinds; they are very sensitive and accurate; their indications can be read at a considerable distance without appreciable error. In conjunction with a Callendar recorder, they will give a complete record of the temperature for a day or a week; if the temperature is read off on a Whipple indicator, no corrections are necessary, as the readings are direct.

THE PRODUCTION OF FERROCYNAGEN FROM GAS-LIQUORS.

By ED. DONATH.

THE method of separating cyanogen known as the wet-method, certainly enables the cyanogen present in the gas to be recovered in a more complete manner than by any other method used up to the present. At the same time, the drawbacks resulting from the presence of cyanogen in the gas-liquors are got rid of, cyanogen being very prejudicial to the elimination of the sulphuretted hydrogen.

However, the old method of purifying the gas is still used, a process by which the cyanogen compounds and the sulphuretted hydrogen are removed simultaneously, and which makes the spent purifying material still the principal source of ferrocyanogen compounds and consequently of cyanogen compounds.

It is true that the amount of cyanogen present in gas-liquors is very small; nevertheless their recovery has occupied the attention of practical men for a long time past. Thus Mr. Bower, in his patent taken out in 1882, recommended the transformation of the cyanides in gas-liquors into ferrocyanides, before distillation with lime, by the addition of iron, and the recovery of these latter salts. In his well-known treatise on "Coal Tar and Ammonia" (3rd edition, page 527), G. Lunge speaks of this patent in an unfavourable manner. However, Mr. Bower's idea has often come up again, and we find in the *Chemische Industrie*, 1897, page 507, the description of a patent by the same H. Bower (English Patent, No. 361, January 6th, 1896), a patent which also has for its object the formation of double cyanides by the addition of iron or of a salt of iron to gas-liquors. These facts have decided me to describe some experiments I undertook in a manufactory of ammonia and ammoniacal salts.

We can see easily that gas-liquors exercise a corrosive action on iron, but this action apparently is more energetic when the water is heated. While the pumps which are used to pump up the cold ammoniacal liquor are corroded but slightly, it is by no means uncommon to observe strong corrosive action on the iron portions of the distilling apparatus. I have even seen, in the works in question, a Feldmann distilling apparatus which had become so completely friable that at many places it was easy to pierce the fairly thick sides with an ordinary knife. A portion removed with a knife consisted principally of graphite and Prussian blue, and it is highly probable that this latter body was formed, thanks to the presence of sulphides in the gas liquors, by the same process as in the purifying material.

In the same works sal-ammoniac was produced for some time by the direct saturation of the ammoniacal waters by raw hydrochloric acid. To precipitate the arsenic and the iron contained in the hydrochloric acid used, the latter was previously treated with a certain quantity of the yellow mother-liquors from the crystallisation, at a low temperature, of the carbonate of ammonium contained in the ammoniacal liquor. These mother-liquors thus contained the most easily soluble ammoniacal compounds; that is to say, the sulphides, the cyanides, and, as was to be expected, the ferrocyanides. It is well understood that this operation was accompanied by a considerable evolution of heat, and sulphuretted hydrogen was given off, but at the same time a dark green mud was formed in quantities by no means negligible. I had occasion to examine this mud, the result of several operations. In the dry state it consisted of a greenish-black powder, with a tarry odour, and was formed principally of Prussian blue accompanied by sulphide of arsenic and tarry products.

After several fruitless attempts, I succeeded in finding a method for the separation and preparation in a state of purity of the Prussian blue contained in this mud. I digested the dry mud with a certain quantity of raw, concentrated hydrochloric acid, which only dissolved the Prussian blue, and left the sulphide of arsenic and the tarry products intact. The hydrochloric solution was filtered through sheep's wool, and it was sufficient to dilute the filtered liquor to completely precipitate the Prussian blue.

The facts of which I have just spoken would hardly be of any commercial value by themselves; but when sal ammoniac is prepared in the manner described, that is to say by the direct saturation of the concentrated ammoniacal liquors, we can recover the cyanogen compounds contained in these liquors, seeing that they gradually accumulate in the yellow mother-liquors referred to above. This recovery can be effected without much difficulty, as the raw, concentrated hydrochloric acid, used for the extraction of the Prussian blue from the mud, will still serve for the preparation of the sal-ammoniac.—*Journ. für Gasbeleuchtung und Wasserversorgung*, vol. xli., p. 880.

CONTRIBUTIONS TO OUR KNOWLEDGE OF
YTTERBIUM.*

By ASTRID CLEVE.
(Continued from p. 253).

III. COMPOUNDS OF YTTERBIUM (continued).

Ytterbium-gold Chloride, $\text{YbCl}_3 \cdot \text{AuCl}_3 \cdot 9\text{H}_2\text{O}$.

CRYSTALLISES in light yellow, transparent, six-sided, deliquescent tables, if a solution of the calculated quantities of ytterbium chloride and acid gold chloride are strongly concentrated over sulphuric acid.

Analysis of the Pressed Salt.

- 0.7633 grm. of the substance gave 0.5281 grm. Yb_2O_3 + Au, of which 0.1198 grm. was Au.
- 0.4259 grm. gave up 0.0552 grm. of water at 100° . From the residue 0.2949 grm. of Yb_2O_3 + Au was obtained.
- 0.2478 grm. of the substance gave 0.3500 grm. AgCl + Au, of which 0.0651 grm. was Au.

	Calculated for $\text{YbCl}_3 \cdot \text{AuCl}_3 \cdot 9\text{H}_2\text{O}$, in per cent.		Found.		
	I.	II.	I.	II.	III.
Yb ..	173.1	23.26	23.47	—	—
Au ..	197.2	26.50	26.2	—	26.3
Cl_6 ..	212.7	28.58	—	—	28.43
$9\text{H}_2\text{O}$..	161.18	21.66	—	—	—

744.18 100.00

Yb_2O_3 + Au .. 69.12 69.19 69.24 —

About 5 molecules of water are lost at 100° ; the calculated loss of weight is 12.11 per cent, and that found (II.) 12.91 per cent.

The erbium compound, $\text{ErCl}_3 \cdot \text{AuCl}_3 \cdot 9\text{H}_2\text{O}$ (Cleve, *Bull. Soc. Chim.*, 1874, xxi., 345), has an exactly similar composition, while the gadolinium (Benedicks, *Zeit. Anorg. Chem.*, xxii., 403) and praseodymium (v. Schéele, "Om Praseodym, &c.," Inaug. Diss., Upsala, 1900, p. 47) compounds contain 10 molecules of water, and the yttrium-gold chloride (*Bull. Soc. Chim.*, 1872, xviii., 198) belongs to the different type $\text{R}^{III}\text{Cl}_3 \cdot 2\text{AuCl}_3 \cdot 16\text{H}_2\text{O}$.

Specific Gravity and Molecular Volume.

- 0.9608 grm., specific gravity 2.857
- 0.9296 " " " " 2.843

Mean value 2.850
Molecular volume .. 261.

Ytterbium-platinum Cyanide, $2\text{Yb}(\text{CN})_3 \cdot 3\text{Pt}(\text{CN})_2 \cdot 18\text{H}_2\text{O}$.

This salt was prepared from ytterbium sulphate and barium-platinum cyanide. It crystallises similarly to the corresponding yttrium compound in perfectly formed prisms, which appear a brilliant red by transmitted light, and green and bluish violet respectively by reflected light. The water of crystallisation was found to amount to 18 molecules, and not to 21, as in the case of the yttrium and erbium salts, according to Cleve (*Bull. Soc. Chim.*, 1872, xviii., 198). Thus the ytterbium compound agrees exactly with that of gadolinium (Benedicks, *loc. cit.*, 406). When dried over sulphuric acid, 16 molecules of water are slowly given up. At 100° the efflorescence of the crystals proceeds more quickly, but 2 molecules of H_2O are still held in combination. When $14\text{H}_2\text{O}$ have passed off the red colour disappears, and the powder becomes brick-yellow and then whitish. It is easily soluble, and resists the action of the air.

Analysis of the Pressed Salt.

- 0.7110 grm. of the substance dried over sulphuric acid suffered a loss of weight of 0.1358 grm.
- 0.3457 grm. of the substance gave 0.2676 grm. Yb_2O_3 + Pt, of which 0.1273 grm. was Pt.

* From the *Zeitschrift für Anorganische Chemie*, xxxii.

	Calculated for $2\text{Yb}(\text{CN})_3 \cdot 3\text{Pt}(\text{CN})_2 \cdot 18\text{H}_2\text{O}$, in per cent.		Found.	
	I.	II.	I.	II.
Yb_2 ..	346.2	22.09	—	22.15
Pt_3 ..	584.4	37.28	—	36.83
$(\text{CN})_{12}$..	312.48	19.93	—	—
$16\text{H}_2\text{O}$..	288.32	18.40	19.06	—
$2\text{H}_2\text{O}$..	36.04	2.30	—	—

1567.44 100.00

Yb_2O_3 + Pt .. 77.76 77.41

Specific Gravity and Molecular Volume.

- 1.0036 grms. (large crystals), sp. gr. 2.661
- 1.1911 " (small crystals), " 2.657
- 1.2100 " (small crystals), " 2.658

Mean value 2.659
Molecular volume .. 589.5

Potassium-ytterbium Ferrocyanide, $\text{KYb}(\text{CN})_6 \cdot \text{Fe} \cdot 3\text{H}_2\text{O}$
(Dried over Sulphuric Acid).

Potassium ferrocyanide gives with solutions of ytterbium chloride the above double salt as a white, fine, granular precipitate, somewhat soluble in excess of the ferrocyanide. After having been dried it has a blue-green tinge, and in the desiccator it retains three molecules of water, one of which it loses at 100° .

Analysis.

- 0.6172 grm. of the substance dried over sulphuric acid suffered a loss in weight of 0.0218 grm. at 100° .
- 0.4546 grm. of the substance dried over sulphuric acid gave, after ignition and extraction with water, 0.2632 grm. Yb_2O_3 + Fe_2O_3 .

	Calculated for $\text{KYb}(\text{CN})_6 \cdot \text{Fe} \cdot 3\text{H}_2\text{O}$, in per cent.		Found.	
	I.	II.	I.	II.
Yb_2O_3 + Fe_2O_3 ..	57.90	—	57.98	—
1 mol. H_2O ..	3.76	—	3.53	—

- 0.2331 grm. of the substance dried at 110° gave 0.1409 grm. Yb_2O_3 + Fe_2O_3 , from which 0.0994 grm. Yb_2O_3 was precipitated from the almost neutral solution by means of oxalic acid. 0.0359 grm. of KCl was obtained from the filtrate.

	Calculated for $\text{KYb}(\text{CN})_6 \cdot \text{Fe} \cdot 2\text{H}_2\text{O}$, in per cent.		Found.
	I.	II.	
Yb ..	173.1	37.58	37.45
K ..	39.15	8.50	8.08
Fe ..	56.10	12.16	12.46
$(\text{CN})_6$..	156.24	33.92	—
$2\text{H}_2\text{O}$..	36.04	11.74	—
	460.53	100.00	

Corresponding double ferrocyanides of yttrium, erbium, and samarium are known (Cleve).

Ytterbium Nitrates.

1. $\text{Yb}_3\text{NO}_3 \cdot 3\text{H}_2\text{O}$.

If a solution of ytterbium nitrate is kept for some months over sulphuric acid, large transparent perfectly-formed tables of the above compound separate out. They are deliquescent.

Analysis of the Pressed Salt.

- 0.6418 grm. of the substance gave, after cautious heating and ignition, 0.3057 grm. Yb_2O_3 .

	Calculated for $\text{Yb}_3\text{NO}_3 \cdot 3\text{H}_2\text{O}$, in per cent.		Found.
	I.	II.	
Yb ..	173.1	41.88	41.83
3NO_3 ..	186.12	45.04	—
$3\text{H}_2\text{O}$..	54.06	13.08	—
	413.28	100.00	

2. $\text{Yb}_2\text{O}_3 + 4\text{H}_2\text{O}$.

Crystallises from concentrated nitric acid in transparent deliquescent prisms. The salt may be obtained, though with more difficulty, by strongly concentrating the aqueous solution; it then forms fine needles.

Analysis of the Pressed Salt.

(a). Crystallised from concentrated nitric acid.

1. 1.0652 grm. of the substance gave 0.4845 grm. Yb_2O_3 .
2. 0.5225 grm. of the substance gave 0.2392 grm. Yb_2O_3 .
3. 0.5141 grm. of the substance gave 80.04 c.c. NO at 0° and 760 m.m. mercury pressure by Schulze's method (*Zeit. Anal. Chem.*, ix., 400).

(b). Crystallised from water.

4. 0.5547 grm. of the substance gave 0.2505 grm. Yb_2O_3 .

	Calculated for $\text{Yb}_2\text{O}_3 + 4\text{H}_2\text{O}$, in per cent.		Found.			
			I.	II.	III.	IV.
Yb ..	173.1	40.14	39.95	40.19	—	39.66
3NO ..	90.12	20.89	—	—	20.89	—
O ₆ ..	96	22.26	—	—	—	—
4H ₂ O ..	72.08	16.71	—	—	—	—
	431.3	100.00				

Specific Gravity and Molecular Volume.—0.7066 grm. of the salt crystallised from nitric acid. Specific gravity, 2.682; molecular volume, 160.9.

All other known nitrates of rare earths contain more water of crystallisation than these two ytterbium compounds, e.g., the yttrium and gadolinium salts crystallise with 5H₂O (Benedicks, *loc. cit.*, p. 407), and the samarium (Cleve, *loc. cit.*, p. 15) and praseodymium (v. Schöefer, *loc. cit.*, p. 52) salts with 6H₂O.

Ytterbium Sulphate, $\text{Yb}_2\text{O}_3 + 8\text{H}_2\text{O}$.

The sulphate has been prepared in the pure state by Nilson and analysed (*loc. cit.*, p. 10). In the cold the salt is considerably more soluble than at higher temperatures, and hence is precipitated on heating cold concentrated solutions.

Crystals prepared in this way contain the same amount of water as the salt which separates out on spontaneous evaporation. The reaction is neutral in solutions which are not too dilute. When very dilute, as will be shown later, hydrolysis begins.

Analysis of the Pressed Substance.

(a). Crystallised at the temperature of the room.

- 2.2041 grms. of the salt gave 1.9779 grms. BaSO_4 .

(b). Crystallised at the temperature of ebullition.

- 1.4054 grms. of the substance gave up 0.2617 grm. H_2O when dried at about 200°.

	Calculated for $\text{Yb}_2\text{O}_3 + 8\text{H}_2\text{O}$, in per cent.		Found.	
			a.	b.
Yb_2O_3 ..	394.2	50.63	—	—
3SO_3 ..	240.18	30.85	30.77	—
$8\text{H}_2\text{O}$..	144.16	18.52	—	18.62
	778.54	100.00		

Specific Gravity and Molecular Volume.

1. 1.2997 grms., temperature 20.6°, sp. gr. 3.30
2. 1.6337 grms., temperature 18.3°, sp. gr. 3.26

Mean value	3.28
Molecular volume	237*

Anhydrous Ytterbium Sulphate, $\text{Yb}_2\text{O}_3 + 3\text{SO}_3$.

1. 1.2292 grms., specific gravity 3.627
2. 1.0947 " " " " " " 3.617

Mean value	3.62
Molecular volume	175*

Determinations of the solubility of the sulphate were made as follows:—The finely powdered anhydrous salt was gradually introduced into a vessel of water until it was present in excess, and was kept in suspension for two to three hours by means of a stirrer. It was kept at the required temperature on a water-bath. Then 25 c.c. of the solution were drawn off, evaporated in a platinum dish, and the residue weighed as anhydrous sulphate.

	Temp.	C.c. solution.	Grms. weight	Grms. $\text{Yb}_2\text{O}_3 + 3\text{SO}_3$.
1.	0°	(a) 25,	35.341,	gave 10.8246
		(b) 25,	35.340,	10.8317
2.	15.5°	25,	32.490,	8.3521
3.	35°	25,	29.490,	4.7393
4.	55°	25,	27.572,	2.8540
5.	60°	25,	27.215,	2.5556
6.	70°	25,	26.410,	1.7796
7.	80°	25,	26.265,	1.7038
8.	90°	(a) 25,	25.914,	1.3968
		(b) 25,	25.930,	1.4593
9.	100°		27.676 grm. solution	1.2346

According to these experiments, 100 parts of water dissolve—

At 0°,	44.2 parts $\text{Yb}_2\text{O}_3 + 3\text{SO}_4$ (mean of 44.15 and 44.21)
" 15.5°	34.6 " "
" 35°	19.1 " "
" 55°	11.5 " "
" 60°	10.4 " "
" 70°	7.22 " "
" 80°	6.93 " "
" 90°	5.83 " (mean of 5.70 and 5.96)
" 100°	4.67 " "

These data show that ytterbium sulphate in the cold possesses a fairly high solubility, which decreases with rising temperature—rapidly to about 70°, and then more slowly. The salt is always considerably more soluble than the sulphates of yttrium and gadolinium; of the compounds most closely allied to it, erbium sulphate surpasses it most in this respect. However, the solubility of the latter is not accurately known, as it was found from material containing ytterbium (Cleve and Höglund, *Bih. K. Vet. Ak. Handl. Stockholm*, 1873, i., No. 8). Some data relating to this point may be given for comparison.

100 parts H_2O dissolve at 0° 3.98 parts $\text{Gd}_2\text{O}_3 + 3\text{SO}_4$ (Benedicks, *loc. cit.*, p. 409).

100 parts H_2O dissolve at temperature of room 43 parts $\text{Er}_2\text{O}_3 + 3\text{SO}_4$.

100 parts H_2O dissolve at temperature of room 1.52 parts $\text{Y}_2\text{O}_3 + 3\text{SO}_4$.

100 parts H_2O dissolve at 100° 10 parts $\text{Er}_2\text{O}_3 + 8\text{H}_2\text{O}$.

100 parts H_2O dissolve at 100° 4.8 parts $\text{Y}_2\text{O}_3 + 8\text{H}_2\text{O}$.

Ytterbium Sulphite, $\text{Yb}_2\text{O}_3 + 9\text{H}_2\text{O}$.

It was prepared by the decomposition, by means of SO_2 , of freshly precipitated carbonate suspended in water. After standing some time over sulphuric acid, the solution, which is filtered if necessary, deposits a white felt-like crust, insoluble in water.

Analysis of the Freshly-prepared Pressed Salt.

0.3490 grm. of the substance gave, after oxidation with chlorine water and precipitation with ammonia, 0.1840 grm. Yb_2O_3 . 0.3189 grm. BaSO_4 was obtained from the filtrate.

	Calculated for $\text{Yb}_2\text{O}_3 + 9\text{H}_2\text{O}$, in per cent.		Found.
Yb_2O_3 ..	394.2	52.56	52.72
3SO_2 ..	192.18	25.67	25.07
$9\text{H}_2\text{O}$..	162.18	21.67	—
	748.56	100.00	

Yttrium, erbium, and samarium sulphites all crystallise with 3H₂O, and the didymium salt with 6H₂O (Cleve).

Ytterbium Hyposulphate.

A solution of the salt, prepared by double decomposition of ytterbium sulphate and barium hyposulphate, thickens on concentration over sulphuric acid to a syrupy consistency, and crystals form in rays. On keeping it in closed tubes, it decomposes after some time, giving up SO_2 .

Ytterbium Ethyl Sulphate, $\text{Yb}_2\cdot 3\text{C}_2\text{H}_5\text{SO}_4 + 9\text{H}_2\text{O}$.

Large, transparent, readily-soluble crystals, obtained from ytterbium sulphate and barium ethyl sulphate. It resists the action of the air; the neutral solution also is stable, but decomposition soon begins in feebly acid solutions. At 70° , alcohol begins to escape; at 160° , it is completely given off at a more rapid rate. Six molecules of water are given up over sulphuric acid.

Analysis of the Pressed Salt.

1. 1.1627 grms. of the substance slowly lost in the desiccator 0.1775 grm., and suffered a further loss of 0.2310 grm. at 160° , and gave 0.5216 grm. $\text{Yb}_2\cdot 3\text{SO}_4$.
2. 0.7928 grm. of the substance gave up 0.1201 grm. of water in the desiccator, and yielded 0.3552 grm. $\text{Yb}_2\cdot 3\text{SO}_4$.

	Calculated for $\text{Yb}_2\cdot 3\text{C}_2\text{H}_5\text{SO}_4 + 9\text{H}_2\text{O}$, in per cent.		Found.	
			I.	II.
Yb ..	173.1	24.36	24.41	24.45
$3\text{C}_2\text{H}_5\text{OH}$	138.18	19.45	19.86	—
			(Loss of wt. at 160°).	
3HSO_4 ..	291.21	40.98	—	—
$6\text{H}_2\text{O}$..	108.12	15.21	15.27	15.15
			(Loss of wt. in desiccator).	
	710.61	100.00		

Specific Gravity and Molecular Volume.—1.1477 grms. Specific gravity, 2.024; molecular volume, 351.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 6, 1902.

Professor McLEOD, F.R.S., Vice-President, in the Chair.

(Concluded from p. 265).

152. "*Di-indigotin*." By J. MOIR, M.A., D.Sc.

The author's object in the following experiments was to prepare the diphenyl analogue of indigotin, in order to ascertain what influence the doubling of the molecule would have on the colour, since this exercises a marked influence in the case of the benzidine dyes as compared with ordinary azo-dyes derived from aniline. Although successful in preparing the new substance, the yield was so poor and its properties so troublesome to investigate that only a meagre description of it is possible.

The method consisted in applying the synthesis of indigo employed by F. Baeyer and Co. to benzidine-dicarboxylic acid instead of to anthranilic acid.

4 : 4'-Benzidine-3 : 3'-dicarboxylic acid was prepared from *o*-nitrobenzoic acid by reduction with sodium hydroxide and aluminium powder until the solution, which was at first dark red, became paler by the conversion of azo- to hydrazo-acid; it was then precipitated with excess of acetic acid, and the hydrazo acid thus obtained boiled with strong hydrochloric acid to convert it into the benzidine derivative, which was obtained on dilution as an almost insoluble powder, coloured pale green

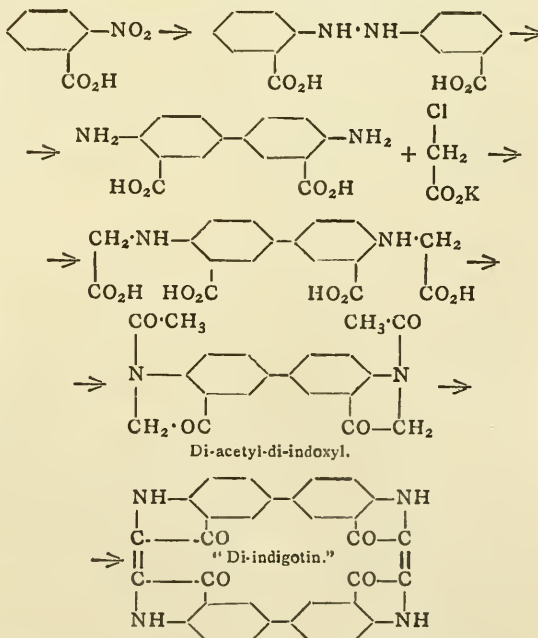
by some oxidation product which could not be removed. It was dissolved in the smallest possible quantity of potassium carbonate solution and mixed with excess of neutral potassium monochloracetate solution. On boiling the mixture for some hours, a small quantity of a crystalline precipitate was obtained, which was filtered off and dried. It melted above 300° and is probably bisphenylglycine-*o*-carboxylic acid,—



This was boiled during four hours with excess of acetic anhydride and dry potassium acetate, and finally taken to dryness on the water-bath. This process closes the indoxyl ring. The product freed from inorganic substances by washing, on digestion with dilute sodium hydroxide, dissolved, the solution becoming green, whilst a pellicle of the di-indigotin formed on the surface. Air was passed into the diluted solution, and the olive-green substance was filtered off, washed, and dried. The filtrate was also dark green and gave on acidifying a dark green carboxylic acid, which probably results from the formation of the indoxyl ring at one end only of the first substance.

The properties of the di-indigotin precluded any exact investigation. It is only very slightly soluble in boiling *p*-toluidine, giving a solution distinctly bluer than the original substance as first prepared in fine suspension. It gives an olive-green solution in concentrated sulphuric acid, but is apparently not sulphonated at 100° . It was not analysed, because it was impossible to guarantee its uniformity, but its stability precludes the possibility that it is merely a substituted indigotin.

The following scheme probably represents its formation:—



An attempt to confirm this by obtaining the same substance by another synthesis was made. All the methods involving potash fusion failed, but the method of Blank (*Ber.*, 1898, xxxi., 1816) was partially successful, and is here given as involving the preparation of a new substance. Benzidine was heated with a solution of half its weight of diethyl bromomalonate in chloroform until the

odour of the former had gone; the product was boiled out with chloroform and benzene, and the filtered extracts concentrated and cautiously treated with ligroin, when the new ester crystallised out in plates. After two re-crystallisations from ethyl acetate, it was white and melted sharply at 138°. An analysis showed it to be the expected *ethyl benzidino dimalonate*,—



0.1564 gave 0.3542 CO₂ and 0.0918 H₂O. C=61.73; H=6.52.

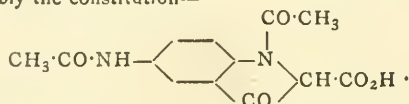
0.2562 gave 12.80 c.c. moist nitrogen at 21° and 759 m.m. N=5.69.

C₂₆H₃₂O₈N₂ requires C=62.40, H=6.40, N=5.60%.

It forms minute lustrous plates, sparingly soluble in alcohol and in cold benzene, easily so in hot benzene, ethyl acetate, and chloroform. It is slowly hydrolysed by alkalis, the solution giving, with acids, a flocculent precipitate of the corresponding acid.

On the analogy of Blank's indigo synthesis from ethyl anilinomalonate, the new ester was heated to 200° in an oil-bath until the evolution of vapour ceased. The product was dissolved in a little acetone, filtered, and precipitated by alcohol, giving a dark gum (whilst the alcoholic solution gave a little of the unchanged substance in needles, identified by mixed melting-point). On boiling the gum with alcohol, a red resin was left, and the alcoholic solution was concentrated and hydrolysed by sodium hydroxide, giving a deep green solution, but no other evidence of the presence of di-indigotin in solid form. Evidently the action of heat on ethyl benzidino-dimalonate is not analogous to its action on ethyl anilinomalonate, for many other temperatures than 200° were tried, but with even less success.

The author has prepared another new substance by boiling benzidine dicarboxylic acid with dry chloroacetic acid and dry potassium chloroacetate; carbon dioxide was split off, but the product was acetylated as in the former synthesis. A crystalline carboxylic acid (lance-shaped white crystals, m.p. 292°) was isolated and re-crystallised from boiling ethyl acetate. Analysis showed C=64.94, H=4.85, N=7.91, hence the formula C₁₉H₁₆O₅N₂, and probably the constitution—



153. "Note on the Localisation of Phosphates in the Sugar-cane." By C. H. G. SPRANKLING.

As very little work has been done with regard to the position of mineral constituents in plants, the author selected the sugar-cane as a convenient plant to ascertain the position of the phosphates therein.

Equal portions of three sound canes were thoroughly dried, and after being ground to a fine powder, weighed quantities were ignited, using a slight modification of Fluckiger's method (*Zeit. Anal. Chem.*, 1889, xxvii., 637).

The ash in each case was extracted with dilute nitric acid, and the final ignited residue taken to be silica; the phosphates in the nitric acid solution were estimated.

From the results of his experiments, the author draws the following conclusions:—

(a). Phosphates are immediately absorbed by the roots of the plant.

(b). These phosphates are rapidly transferred to the upper parts of the plant.

(c). A quantity of phosphates is stored in the upper portions and leaves of the cane.

(d). The silica is transferred regularly to the leaves, and there stored.

154. "On the Non-existence of the Gaseous Sulphide of Carbon described by Deninger." By E. J. RUSSELL and N. SMITH.

The authors have examined the gas prepared as Deninger describes (*Journ. für Prakt. Chemie*, 1895, [2], li., 346), and to which he gave the formula CS. Deninger prepared it (1) by heating together in a sealed tube chloroform and sodium sulphide, (2) by subjecting to the same treatment a mixture of iodoform and silver sulphide, (3) by the action of sodium on carbon disulphide mixed with aniline. The authors can find no evidence whatever of the existence of this gas. Sodium and carbon disulphide left in a closed apparatus fitted with a mercury gauge were found to produce no gaseous substance; a mixture of sodium, aniline, and carbon disulphide evolved hydrogen and hydrogen sulphide, and these gases in escaping carried over some carbon disulphide. Evidence that no other gas was present was obtained (1) by analysis, (2) by cooling the mixture and separating it into its constituents.

On heating together in a sealed tube to 180° a mixture of potassium sulphide and chloroform, the products were hydrogen sulphide, hydrogen chloride, chloroform, a reddish-yellow liquid which was apparently an alkyl sulphide, and free sulphur. A mixture of iodoform and silver sulphide similarly treated yielded hydrogen, carbon disulphide, and the reddish-yellow liquid. Although owing to the complex nature of these products the authors can hardly assert that no new gas having the formula CS was present, they could find no indication of any such compound.

155. "Hydroxyoxamides." Part II. By R. H. PICKARD, C. ALLEN, W. A. BOWDLER, and W. CARTER.

The authors described the following new hydroxyoxamides, namely:—*o*-, *m*-, and *p*-nitrophenyl-, *o*-tolyl-, and ethyl-hydroxyoxamides. These react as hydroxamic acids (*Trans.*, 1901, lxxix., 841). The esters of hydroxyoxamides are weak acids, and the hydroxyoxamides react with phenylhydrazine, forming phenylhydrazides. These and other reactions show that the hydroxyoxamides behave like typical hydroxamic acids, and are therefore constituted according to the formula R·NH·CO·C(OH):NOH and not R·NH·C:(NOH)·CO₂H, as suggested by Schiff (*Annalen*, 1902, cccxxi., 357) and Hollemann (*Rec. Trav. Chim.*, 1896, xv., 148).

156. "Isometric Anhydrous Sulphates of the Form M'SO₄, R₂'SO₄." By F. R. MALLET.

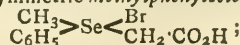
The author described the anhydrous salts MgSO₄, K₂SO₄, MgSO₄, Rb₂SO₄, MnSO₄, K₂SO₄, MnSO₄, Rb₂SO₄, MnSO₄, Tl₂SO₄, NiSO₄, K₂SO₄, and CoSO₄, K₂SO₄, which all crystallise in tetrahedral forms, being allied in this respect to the sulphates 2M'SO₄, R₂'SO₄ previously described (*Trans.*, 1900, lxxvii., 216). They vary in their stability when exposed to the air, some remaining unaltered, whilst others are converted somewhat rapidly into the hexahydrated salts, M'SO₄, R₂'SO₄·6H₂O.

157. "The Catalytic Racemisation of Amygdalin." By J. W. WALKER.

Much more amygdalin is dissolved by water containing a small quantity of alkali, of alkaline earth, or of alkali carbonate, than by pure water. From polarimetric determinations of the rate of hydrolysis of the various substances involved, the author concludes that in alkaline solution the glucoside is racemised by the catalytic action of the hydroxyl ions, and that amygdalinic acid is racemoid with respect to its asymmetric carbon atom.

158. "On Asymmetric Optically Active Selenium Compounds and on the Sexavalency of Selenium and Sulphur." By W. J. POPE, F.R.S., and A. NEVILLE, B.Sc.

Methylphenyl selenide, C₆H₅·Se·CH₃, the first mixed alkyl selenide which has been described, is obtained as a pale yellow oil boiling at 200–201° by the action of methyl iodide on the sodiophenyl selenide of Krafft and Lyons. Owing, apparently, to the highly basic character of selenium, it differs markedly from methylphenyl sulphide in that it combines readily with bromoacetic acid to form the asymmetric *methylphenylselenetine bromide*,—



this salt crystallises in colourless scales melting at 111° , and on treatment with silver *d*-bromocamphorsulphonate, yields a mixture of the two following salts, which may be separated by crystallisation from alcohol.

d-Methylphenylselenetine *d*-bromocamphorsulphonate (*d*-B, *d*-A), $\text{Se}(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{C}_{10}\text{H}_{14}\text{BrOSO}_3$, is the less readily soluble, and forms needles melting at 168° ; in aqueous solution, its rotations are $[\alpha]_D = +61\cdot26^{\circ}$ and $[\text{M}]_D = +330\cdot8^{\circ}$.

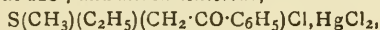
l-Methylphenylselenetine *d*-bromocamphorsulphonate (*l*-B, *d*-A), is much more soluble than the preceding salt, and is obtained in minute white scales melting at 151° . Its rotations in aqueous solution are $[\alpha]_D = +38\cdot81^{\circ}$ and $[\text{M}]_D = +209\cdot6^{\circ}$. Since the *d*-bromocamphorsulphonic ion has the molecular rotation $[\text{M}]_D = +270^{\circ}$, the corresponding value for the optically active selenetine ion is $[\text{M}]_D = \pm 60\cdot6^{\circ}$.

The *dextro*- and *laevo*-methylphenylselenetine platinochlorides, $[\text{Se}(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{CH}_2\cdot\text{CO}_2\text{H})\text{Cl}]_2\text{PtCl}_4$, form yellow prisms melting at 171° ; they have the molecular rotations $[\text{M}]_D = +55\cdot0^{\circ}$ and $-54\cdot3^{\circ}$ respectively in acetone solution.

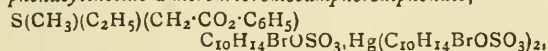
The same optically inactive methylphenylselenetine mercuriodide, $\text{Se}(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{CH}_2\cdot\text{CO}_2\text{H})\text{I}\cdot\text{HgI}_2$, is obtained by precipitating either of the salts (*d*-B, *d*-A) (*l*-B, *d*-A), or methylphenylselenetine bromide with a solution of potassium mercuric iodide; the mercuriodide forms white scales melting at 141 – 142° . The optical inactivity of this salt being remarkable, in view of the fact that the *d*- and *l*-benzylphenylallyl-methylammonium ions preserve their optical activity during formation of the mercuriodides, it seemed desirable to ascertain if the same behaviour was exhibited during the formation of a mercuriodide from an optically active thetine.

The authors therefore prepared the optically active methylethylphenacylthetine salts of Smiles instead of the methylethylthetine compounds previously described by Pope and Peachey, owing to the greater optical rotations exhibited by the optically active ions of the former substances. It was then found that the *d*-methylethylphenacylthetine *d*-bromocamphorsulphonate, (*d*-B, *d*-A), had the molecular rotation $[\text{M}]_D = +332\cdot8^{\circ}$, whilst the corresponding salt (*l*-B, *d*-A), gave $[\text{M}]_D = +210\cdot6^{\circ}$; the optically active methylethylphenacylthetine ion therefore has the molecular rotation $[\text{M}]_D = \pm 61\cdot1^{\circ}$, a value about three times as great as $[\text{M}]_D = \pm 19\cdot4^{\circ}$, the molecular rotation deduced from Smiles' determinations.

Each of the above salts yields the same optically inactive mercuriodide, $\text{S}(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5)\text{I}\cdot\text{HgI}_2$, melting at 128° , and mercurichloride,—



melting at 119° . They also give the same methylethylphenacylthetine-*d*-mercuribromocamphorsulphonate,—



which has a molecular rotation $[\text{M}]_D = +799^{\circ}$, very nearly three times that of the *d*-bromocamphorsulphonic ion, and in which the sulphur atom does not seem to act as a centre of optical activity.

The authors conclude that the mercuri-compounds of the sulphonium and selenonium bases probably contain sexavalent sulphur and selenium.

159. "The Transformation of Acetylchloroaminobenzenes into the Isomeric Chloroacetanilides." By F. D. CHATTAWAY and K. J. P. ORTON.

Owing to the recent publication by Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, p. 178) of measurements of the velocity of transformation of acetylchloroaminobenzene into *p*-chloroacetanilide, the authors wish to record the results of some preliminary experiments made by them two years ago (September, 1900) on isomeric changes of this type. These experiments were not published at that time, as Armstrong had previously stated (*Trans.*, 1900, lxxviii., 1053) that he was engaged on a similar investigation.

To follow the course of the isomeric change, a 1 per cent solution of the chloramine in glacial acetic acid or in 50 per cent acetic acid was kept at a constant temperature in the dark, and the amount transformed estimated at intervals by titrating the iodine liberated from hydriodic acid by the unchanged substance. In the presence of an acid, such as hydrochloric or sulphuric, the isomeric chloroacetanilide is produced. When hydrochloric acid is added, the change starts at once, and proceeds regularly; with sulphuric acid, on the other hand, no transformation occurs at first, but after a short interval it begins and proceeds at a constantly increasing rate. At any period, however, during which isomeric change is taking place, hydrogen chloride can be recognised in the solution. The results of the authors confirm the observation first made by Armstrong (*loc. cit.*), that hydrochloric acid has a specific action in the transformation of phenylchloramines.

The experiments were carried out mainly with acetylchloroamino-*p*-chlorobenzene, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NCl}\cdot\text{Ac}$, not only because this substance is obtained somewhat more easily in a pure state, but especially because it changes more slowly into the isomeric anilide than does acetylchloroaminobenzene.

The value of the velocity coefficient, calculated from the equation $k = 1/t \log a/(a-x)$, increases with the amount of the catalytic agent and with the temperature, but decreases when the proportion of water in the solvent is increased. In any given experiment, it also begins to increase at some point in the course of the reaction, usually after the first 50 per cent of the chloramine has changed.

The following experiment shows the kind of results obtained:—A 1 per cent solution of acetylchloroamino-*p*-chlorobenzene in glacial acetic acid containing 0.023 per cent hydrogen chloride was kept at a temperature of $16\cdot5^{\circ}$, and the unchanged chloramine estimated at the end of one, two, four, six, eight, twenty-four, and twenty-eight hours. Calculating the velocity coefficient from the above equation, the values obtained are respectively 0.0100, 0.0104, 0.0106, 0.0105, 0.0107, 0.0109, and 0.0110; the mean value is 0.0106.

In a series of experiments carried out in order to ascertain the effect of temperature and of variation in the percentage of hydrogen chloride present, and in the concentration of the acetic acid, the following results were obtained:—Using a 1 per cent solution in glacial acetic acid containing 0.023 per cent hydrogen chloride, half the chloramine was transformed in 27.4 hours; but in the presence of 0.069 per cent hydrogen chloride, half was transformed in 5.33 hours, the temperature in each case being $16\cdot5^{\circ}$. With a 1 per cent solution containing 0.023 per cent hydrogen chloride, at a temperature of $35\cdot9^{\circ}$, half was transformed in 2.75 hours; the value of the velocity-coefficient in this case was not constant, but rapidly increased. Using 50 per cent acetic acid containing 0.023 per cent hydrogen chloride as the solvent, 120 hours elapsed before half was transformed at a temperature of $16\cdot5^{\circ}$.

With 0.9 per cent sulphuric acid, instead of hydrogen chloride, in glacial acetic acid, at a temperature of $16\cdot5^{\circ}$, no appreciable change occurred in two hours; but after twenty-four hours 8.9 per cent, and after eighty-four hours 50 per cent had changed. Hydrochloric acid, which could not be recognised in the solution after two hours, was found to be present after twenty-four hours.

Similar experiments made with acetylchloroaminobenzene, $\text{PhNCl}\cdot\text{Ac}$, show that the isomeric change takes place at a greater rate when the chlorine can wander into the para-position than when it can only pass into the ortho-positions. Thus, in an experiment similar to those just described ($\text{HCl} = 0.023$ per cent), the time required for the transformation of half the chloramine was two hours instead of 27.4 hours.

In connection with the transformation of phenylacetylchloramines under the influence of hydrogen chloride, the following facts are worthy of note:—When kept in the dark at the ordinary temperature, the titer of a solution in

glacial acetic acid of acetylchloroamino-2:4-dichlorobenzene, which under these conditions cannot be transformed into the isomeric *s*-trichloroacetanilide, slowly falls, and at the same time a vapour (probably hypochlorous acid) is given off, which sets free iodine from potassium iodide. (A similar vapour is evolved from solution of any chloramine in glacial acetic acid). If small quantities of hydrogen chloride or sulphuric acid be present, the titer decreases more rapidly; thus with a solution of the last-mentioned chloramine containing 0.069 per cent of hydrogen chloride, the titer fell 23 per cent at 16.5° in eight days, whilst in the presence of 0.36 per cent sulphuric acid the titer fell 8 per cent of the initial amount in the same period. In both cases the solutions, which were kept in the dark, acquired a yellow colour. Possibly these changes are due to the hydrolysis of the chloramine; the acetic acid contained 1.8 per cent of water. Further, when a solution of hydrogen chloride in dry petroleum is added to a solution of acetylchloroamino-*p*-chlorobenzene in the same solvent, *p*-chloroacetanilide, which is insoluble in petroleum, immediately separates.

Blankensma (*loc. cit.*) has drawn attention to the action of light in effecting this isomeric change, and has observed the transformation of the solid substances under its influence. On exposing any chloramine dissolved in chloroform or in acetic acid to sunlight, the originally colourless solution in a few minutes becomes yellow, and acquires a chlorous smell; in all cases the solution then gives a precipitate with silver nitrate. If a phenylacetylchloramine, which is capable of isomeric change, is so treated, transformation follows. Thus after two hours' exposure to sunlight, acetylchloroamino-*p*-chlorobenzene is changed into the isomeric anilide to the extent of 31 per cent when dissolved in chloroform, but only to the extent of 12 per cent when dissolved in acetic acid. The light is probably active by virtue of the fact that it induces decomposition, in the course of which the catalytic agent is formed.

These results show that in the presence of hydrogen chloride the transformation of phenylacetylchloramines into chloroanilide is apparently a monomolecular reaction, and in this way resembles other similar isomeric changes; but it must not be forgotten that in measuring the speed of a chemical reaction the velocity of the slowest of the series of simple changes which constitute the complete transformation is alone measured.

NOTICES OF BOOKS.

The Analysis of Steel Works Materials. By HARRY BREARLEY and FRED. IBBOTSON. London, New York, and Bombay: Longmans, Green, and Co. 1902.

THE importance of a book of this type, which represents the scientific knowledge and experience of thoroughly practical men, can hardly be over-estimated. Too often we have brought before our notice books in which either the practical applications and details are excellent, while the scientific explanations are slovenly or glaringly inaccurate; or the reverse holds good, and methods are advocated which, though excellent from the point of view of a difficult exercise in pure science, are utterly impracticable and absurd from a practical point of view, when the time occupied by the processes, and the intricacy and elaborateness of the apparatus necessary for them are taken into consideration. Such details as economy of time, space, and apparatus are of very great importance in works' laboratories, and have evidently been kept well before the minds of the authors. Undoubtedly, in some cases the complexion of the book reflects, and that very vividly, "personal prejudices." At the same time, it is to be remembered that the prejudices of such authorities as the authors are in all probability well grounded, and less experienced men will gladly avail themselves of the knowledge of those who have had unique opportunities of

acquiring experience and skill. Before passing to a detailed description of the contents of the book, we must relieve ourselves of a word of complaint as to the form into which some of the statements are thrown; a little care would have sufficed to polish some of the sentences, and would have infinitely improved the general style, a by no means insignificant object even in the region of science and laboratories. Careful proof-reading should not have passed by many errors in grammar and orthography which disfigure some pages.

The book is divided into thirteen parts. The first deals with the estimation of all ordinary constituents of steel. The methods described for the determination of carbon do not include the Eggertz colour test, which the authors regard as an accurate method "only under ideal conditions." This is a valuable expression of opinion coming from such a source, since this method has generally been regarded as trustworthy and exact. Methods of distinguishing or estimating the four different modifications of carbon recognised by Ledebur are given from his "Leitfaden für Eisenhütten-Laboratorien." In the case of sulphur, Ledebur's bromine process is apparently considered to be superseded, but a useful and conveniently quick volumetric method is described in detail. Naturally, a great number of methods of estimation of phosphorus are tabulated and described; we may point out that in this as in some other cases the authors appear to somewhat under-estimate the time some of the processes would take; for instance, thirty phosphorus estimations in one day by the method specified appears to be an enormous number, though it is specially stated that this is a task which could not be regularly discharged by one person. In the case of nickel, the authors do not advocate the employment of electrolytic methods of separation and determination, the usefulness and convenience of which they think are, generally speaking, very much over-rated; this opinion we cannot help thinking they will sooner or later see reason to modify. A couple of pages are next devoted to such few methods for the analysis of pig-irons as are not generally employed in steel analysis. Part III. deals with the steel-making alloys; in the case of silicon, special methods are given for the recently introduced high-grade alloys. The determinations of these alloys are most thorough and explicit in all cases, and useful typical results of analyses are added. Short accounts of methods of rapid analysis at the furnace are next given, *i.e.*, processes which are fairly accurate, and in most cases only occupy a few minutes. Such methods of course only aim at approximate results, but those advocated by the authors have certainly the merit of great rapidity; in some cases the time each operation takes is mentioned, and appears to be well within the limits of any possible requirements. Part V. treats of the analysis of iron, manganese, tungsten, and chromium ores, somewhat briefly described. Parts VI. and VII. are devoted to the analysis of various refractory materials, such as ganister, silica bricks, &c., and a few special methods for slags. Fuel is somewhat sketchily treated, the methods of gas analysis being only very briefly indicated. A further development of this section would enhance the usefulness of the book, and render a future edition more complete. Part IX. deals with boiler-water, boiler-scales, &c. Clarke's process for the determination of the hardness of water, although described, is mentioned as rapidly and deservedly growing obsolete, Hehner's method being regarded as more generally useful. For the prevention of scale formation the determination of the necessary amounts of precipitants used is discussed at some length; Kalmann's paper on Béranger and Stingl's method of softening water being abstracted. In Part X. the analysis of engineering alloys is treated more fully than is usual in books of this kind; the methods given are invariably as simple as possible, and typical examples are always employed, so that by the help of this section the analyst should be able to cope with almost any alloy that may come in his way. An excellent section on the micro-

graphic analysis of steel will undoubtedly be exceedingly useful, instructions for the preparation of samples being fully given, and valuable illustrations of various steels reproduced; these are mostly prepared from specimens belonging to the Metallurgical Department of University College, Sheffield. In connection with this part of the subject, the micro-structure of hardened steel receives special attention, the opinions expressed being confessedly at variance with those generally entertained; the authors' views must of course be judged on their own merits; at any rate they are clearly expressed, and are the results of personal observations and experiments. A short chapter on "Pyrometry" has been specially written for the book by Mr. A. McWilliam, A.R.S.M. Short miscellaneous notes on various subjects embody many practical hints regarding details of manipulation, &c.; these include an abstract of a paper by Franz Hundeshagen on "Phosphododecamolybdic Acid, the Conditions of its Formation, and its Separation as an Ammonium Salt."

A lengthy appendix gives a bibliography of steel-works' analysis, compiled by one of the authors. Various parts of this have already been published in the CHEMICAL NEWS; these are now collected and brought up to the end of the year 1901, making a most useful addition to the volume.

The Electro-plating and Electro-refining of Metals. Being a New Edition of Alexander Watts's "Electro-deposition." Revised and largely Re-written by ARNOLD PHILIP, A.R.S.M., B.Sc., &c. With numerous Illustrations. London: Crosby Lockwood and Son. 1902. Pp. 680.

THIS new edition of Alexander Watts's book on Electro-deposition, appears under a new title, and is divided into two principal parts: Part I. "On Electro-plating," and Part II. "On Electro-metallurgy." It would appear, however, that even this latter sub-title requires modification, inasmuch as the whole of the subject of the electrical extraction of metals from their ores—with the exception of the electrolytic smelting of aluminium—has been excluded from the book, principally, as the author tells us, on account of the unsatisfactory state in which this portion of electro-metallurgical technology still exists.

One of the first impressions given by this volume is its great scope; the amount of matter included is very large, as may be judged from the fact that Part I. consists of twenty-eight chapters and an appendix in two parts, and Part II. contains eight chapters and fourteen useful tables.

After a few chapters on primary and secondary batteries, thermopiles, dynamos, and electro-plating installations, the author gives a short historical review of electro-deposition, followed by five chapters on the practical electro-deposition of copper, in which this important subject is dealt with in a thorough and masterly manner.

Then follow chapters on the electro-deposition of gold, mercury, silver, nickel, tin, and other metals, including many alloys.

Part II. commences with a historical review of the electro-metallurgy of copper; Chapters II. and III. deal with the cost of electrolytic copper refining, current density as a factor in profits, and some important details in electrolytic copper refineries. These two chapters are of an eminently practical nature, and should be carefully studied by copper refiners.

There are several chapters on the electro-refining of other metals, such as gold, silver, lead, nickel, &c.; while Chapter VIII. is on electro-galvanising, or the electro-deposition of zinc on iron, which is the only successfully practised process for the electrolytic treatment of zinc.

The index has been carefully compiled, and is divided into two sections, viz., a subject index and an index of names.

Seventh Annual Report (for 1900) on Field Experiments on the Manuring of Vegetable and Fruit Crops. Carried out with the Co-operation of Mr. F. W. E. SHRIVELL at Golden Green, Hadlow, Tonbridge. By Dr. BERNARD DYER. London: Vinton and Co., Ltd. 1902. Pp. 88.

THE seventh experimental year, 1900, on the whole, was a successful one. The experiments on various vegetables and fruits were continued, the latter ones having assumed important dimensions; besides these, an experimental apple orchard has been established, of one acre in extent, divided into six plots, each of which contains a number of varieties of apples.

As in the last report, Dr. Dyer gives under each crop, not only the results of the experiments for the year under consideration, but also a general summary of the collective results of the experience gained with such crop during the seven years of the experimental work.

As has been stated in previous reports, the soil of the main experimental field is a poor clay loam, resting on a deep bed of heavy clay, and is therefore an excellent soil for the purposes of experiment; the result of the spade culture and of assiduous manuring has been to convert the field into a fertile market garden.

The results of seven years' experience has been, to put it briefly, that in nearly every case the advantages obtained by heavy dressings of dung, as so often used, can be obtained sufficiently well and with greater economy by the use of smaller dressings of dung, supplemented with a sufficient quantity of chemical fertiliser to supply a proper quantity of plant food. Full details of the experiments will be found in the pamphlet.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 19, November 10, 1902.

Artificial Preparation of Rubies by means of Fusion.—A. Verneuil.—Up to the present time the preparation of artificial rubies has not been successful. The author finds that certain conditions have to be fulfilled in order to prepare aluminium in a transparent form. (1) The melted product must be kept in exactly the same region of the flame; (2) the materials must be packed in thin layers alternately; (3) the points of contact between the melted product and the support should be reduced to as small an area as possible. When these conditions are fulfilled rubies are prepared of a magnificent red fluorescence, of density 4.01. These are found to have the same hardness as natural rubies and to take a good polish. There are, however, often defects in their structure which show their artificial origin, one of these being the presence of different coloured zones due to the decolouration of certain portions.

Alloys of Copper and Magnesium.—O. Boudouard.—Alloys of copper and magnesium keep their white colour more or less brilliant until the copper attains a percentage of 70, when the alloys take a faint yellowish tinge. An 80 per cent alloy is yellowish and a 90 per cent one deep yellow. An alloy of 10 per cent copper is malleable; above this it becomes brittle and this property increases until a 70 per cent alloy is reached. Such a substance can then be broken with the fingers. The fragility after this decreases until pure copper is attained. The author, in a series of experiments, compares the various properties of these alloys of magnesium with the corresponding ones of aluminium.

The presence of Volemite in certain Primulas.—J. Bougault and G. Allard.—The authors isolated a com-

pound from *Primula grandiflora* which is crystalline and has the properties of a polyatomic alcohol; to this they gave the name of primulite. Further examination, however, shows that it can be identified with volemite, the heptatomic alcohol which Bourquelot discovered in *Lactarius volemus*. The authors now describe the method by which this product may be isolated, and investigate its properties. Its empirical formula is $C_7H_{16}O_7$.

Chemical Constitution of Copals.—Marcel Guérdras. —The author's investigations are carried out on the oil obtained during the pyrogenation of copals in order to render them soluble for the manufacture of varnish. Three varieties of gum are used:—(1) Copal of Madagascar; (2) copal of Zanzibar; (3) copal of Kausi. He finds in all cases that the purer the copal the larger the quantity of acid. The oils are soluble in alcohol, ether, benzene, and carbon disulphide, but insoluble in the terebenic carbides. When they are treated with nitric acid, a yellow resin is obtained soluble in the solvents mentioned above and also in vegetable oils. They have not, however, succeeded in isolating either cinnamic or benzoic acid or their nitrated derivatives from these oils. The characteristic odour of terpene during the distillation of the oil when oxidised with nitric acid, and the presence of oily globules with an odour of camphor are probably due to the formation of mono-chlorhydrate of terebenthene, $C_{10}H_{16}HCl$, which leads the author to suppose that the copals are in part constituted by the terpenes in certain degrees of oxidation.

MISCELLANEOUS

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., Sir James Crichton-Brown, Treasurer and Vice-President, in the Chair. The following were elected Members:—Edward Divers, M.D., Miss Amy French, Winifred, Lady Howard of Glossop, and Mr. J. H. Whitehorn. The special thanks of the Members were returned to Mrs. Hickman for her donation of £21, and to Dr. Frank McClean, F.R.S., for his donation of £40 to the Fund for the Promotion of Experimental Research at Low Temperatures.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.—Society of Arts, 8. (Cantor Lectures). "The Future of Coal-gas and Allied Illuminants," by Prof. Vivian B. Lewes.
- WEDNESDAY, 10th.—Society of Arts, 8. "French Rural Education and its Lessons for England," by Clouesley Brereton.
- THURSDAY, 11th.—Society of Arts, 4.30. "Domestic Life in Persia," by Miss Ella C. Sykes.
- FRIDAY, 12th.—Physical, 5. "A Portable Capillary Electrometer," by S. W. J. Smith. "On Astigmatic Aberration," by R. J. Sower. "Experiments on Shadows in an Astigmatic Beam," by Prof. S. P. Thompson. "A Lecture Experiment on Gaseous Diffusion," by Prof. L. R. Wilberforce. "Vapour-density Determinations," by Prof. Sir W. Ramsay, F.R.S., and Dr. B. B. Steele.

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PHYSIOLOGICAL HISTOLOGY:

METHODS AND THEORY

BY

GUSTAV MANN,

M.D., C.M. EDIN.; B.SC. OXON.;

Senior Demonstrator of Physiology, University of Oxford.

CONTENTS.—Definition of Histology.—Discussion as to Value of Fixation.—Physical Chemistry.—Colloids and Coagulation.—Chemistry of Reagents used in Fixation.—Formulae of the more important Fixing Fluids.—The Macroscopical Effects of Fixing Reagents.—Microscopical Phenomena of Coagulation and Precipitation.—Guide to the Selection of a Fixative.—Application of Fixatives to Tissues.—On Bleaching, Isolating, and Decalcifying.—On Injecting blood and Lymph Vessels.—Methods of obtaining Sections.—Microtomes.—General Remarks on the Nature of Dyes.—The History of Staining.—Classification of Staining Methods.—Physical Methods of Staining.—Chemical Methods of Staining.—Chemical Methods. Staining after Mordanting.—Staining after Impregnation with Protein and other Substances.—Impregnation Methods.—On the Chemistry of some Tissue Constituents.—Micro-chemical Reactions.—The Theory of Staining.—How to render Preparations Permanent. **APPENDIX:**—The Chemistry of Dyes. **ADDITIONAL NOTES:**—I. Micro-anatomical Reactions.—II. On Staining.—Electrical Measures.—Tables of Measures and Weights.—Measures of Temperature. **INDEX.**

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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2246.

INFUSORIAL EARTH IN IRELAND.

By Dr. T. L. PHIPSON.

A DIATOMACEOUS deposit of considerable extent has been discovered in County Antrim, Ireland, and a specimen was recently sent to me for analysis; the owners of the property on which it was found thinking it was a kind of clay or kaolin.

The microscopic examination at once revealed its real nature, and my analysis gave the following results:—

Water	10.00
Organic matter and combined water ..	5.02
Oxide of iron and alumina	4.99
Lime, magnesia, and alkalis (chiefly lime)	1.20
Silica	78.79
	100.00

When moist it is of a light brown colour, but when dried it is almost quite white. The organic matter shows crenic or apocrenic acid.

The diatoms in this earth are remarkably large and beautiful.

In former years I have noticed that flour is sometimes adulterated with this substance on the Continent, and as this fraud is so easily detected I trust that our Government chemists and others will prevent such flour being used in Great Britain.

Casa Mia Laboratory, Putney,
December 4, 1902.

MODIFICATION OF THE RAPID ESTIMATION OF MANGANESE IN STEEL.

By CHARLES RAMORINO.

THE rapid methods employed at the present time in steel-works for the estimation of manganese in steel are nearly all volumetric, and are modified according to the well-known method devised by Volhard, which gives very precise and satisfactory results.

But the manipulation which has to be undertaken specially with a view to the elimination of the reducing carbonaceous matter, and to oxidise the manganese thoroughly, are very long as a rule, and only a very limited number of analyses can be finished in a day, as each one occupies a good deal of time. The modification I propose is the following one; I have applied it in my laboratory, and the results obtained agree perfectly with those obtained by the other methods in general use:—

Two grms. of the sample of steel, taken by means of a drilling machine, are attacked with 30 c.c. of nitric acid; density, 1.20. The attack takes place suddenly in the cold; the metal is allowed to dissolve until we notice flocculent portions of carbon mixed with iron floating about the surface. The solution is completed by heating over a Bunsen burner, and boiling for some minutes until the fumes of the hyponitrite are completely driven off. Then we carefully pour in 20 c.c. of bromised hydrochloric acid, prepared by mixing 10 c.c. of strong hydrochloric acid, density 1.19, and 10 c.c. of strong bromine water. This is boiled, keeping the beaker covered over with a funnel, and kept at the boiling-point for ten minutes until the expulsion of the bromine fumes is complete. We then dilute the solution with about 200 c.c. of cold distilled

water. The whole is then poured into a flask of one litre capacity, and we add 200 c.c. of boiling distilled water, and 25 grms. of pure precipitated oxide of zinc. This is allowed to settle and titrated permanganate is run in from a burette until the rose-colour is persistent.

Several estimations can be made in from fifteen to twenty minutes.

It is necessary to pay attention to the purity of the oxide of zinc used; the ordinary correction for 25 grms. of oxide may vary in a titration where 1 c.c. = 0.00119 Mn from a half to 1 c.c.—*Moniteur Scientifique*, Series 4, vol. xvi., p. 419.

NOTE ON ISATIN.

By H. J. P. FIRMIN.

WHILE recently preparing a quantity of isatin from indigo by oxidation with nitric acid I made the following observation on separating the resin:—

Most of the resin is precipitated from a strong ammoniacal solution of the resinous and crystalline mass by the cautious addition of diluted hydrochloric acid; the solution filtered, and more acid added till the precipitate shows signs of isatin.

At this point a minute quantity of ammonia is added—with diligent stirring—just sufficient to remove the tendency to a reddish tinge in the precipitate, and the liquid set aside for several days. The resin will precipitate completely without any loss of isatin, and on filtering and adding more acid a most brilliant red precipitate of the latter will occur quite free from resin.

If attempt is made to precipitate all the resin without allowing the solution to stand, either some isatin will come down with the resin, or some of the latter remain with the isatin.

Though in the original mass of resin and crude isatin the former dissolves in ammonia more readily than the latter, yet on precipitating from this solution the resin and some of the isatin with hydrochloric acid, and then, without filtering, adding ammonia, the isatin appears to be taken up before the resin,

It is naturally impossible on paper to describe the exact point at which to add or stop adding the acid or ammonia, but in practice it is soon hit upon.

If a little too much ammonia be added, a trace of acid will put matters right, and *vice versa*.

A CONTRIBUTION TO THE ELECTRO-CHEMISTRY OF BARIUM COMPOUNDS.*

By MAX M. HAFF.

THE recent successful extension of electro-chemical methods to the industrial manufacture of the barium compounds, such as the electric furnace method used by the United Barium Company, has led to renewed interest in the details of such manufacture. For a description of the above-mentioned process I would refer to the paper of Mr. Chas. B. Jacobs, in the *Transactions of the American Inst. of Electrical Engineers* for February 28, 1902. Since the separation of the crystalline barium hydrate in this process, by cooling the solution, is of capital importance to the method of manufacture, I have thought that some carefully determined data as to the freezing-points of such solutions and their specific gravity for differing percentages of hydrate,—as obtained in the course of our laboratory work and practice at Niagara Falls, will be of interest to electro-chemists who are following the developments of this process.

* A Paper read at the Second Meeting of the American Electro-chemical Society, Niagara Falls, September 18, 1902.

Strength of BaH_2O_2 Solutions at 80°C . By Volume and Weight.

Specific gravity.	Per cent BaH_2O_2 . Volume.	Per cent BaH_2O_2 . Weight.
1'514	58'22	38'45
1'500	56'31	37'54
1'479	54'14	36'60
1'458	49'38	33'87
1'450	48'90	33'72
1'413	45'99	32'55
1'400	45'00	32'14
1'390	44'22	31'81
1'375	42'40	30'84
1'368	41'45	30'30
1'350	38'60	28'59
1'338	37'30	27'88
1'312	35'02	26'69
1'301	34'02	26'13
1'278	31'48	24'67
1'249	28'14	22'52
1'236	26'41	21'36
1'219	24'53	20'12
1'200	23'00	19'17
1'195	22'15	18'53
1'174	19'83	16'89
1'152	17'78	15'43
1'129	16'01	14'18
1'125	15'80	14'04
1'114	14'56	13'07
1'100	13'06	11'87
1'076	10'58	9'83
1'062	9'16	8'62
1'049	7'55	7'20
1'040	6'51	6'26
1'031	5'18	5'02
1'022	4'78	4'67
1'015	3'90	3'84
1'009	3'37	3'34

Freezing-point of BaH_2O_2 Solutions.

Per cent BaH_2O_2 .	$^\circ\text{C}$.
54'23	80'0
46'7	78'0
40'7	76'0
32'7	73'0
31'3	72'2
28'6	70'3
27'1	69'2
25'6	68'1
24'0	66'7
22'4	65'3
20'6	63'4
18'4	60'6
16'9	58'8
14'8	55'0
12'0	47'6
10'4	42'7
8'2	34'5
7'0	30'0
4'8	20'0
3'0	9'5
2'25	5'0 (a)
1'75	0'0 (b)

(a) Saturated solution at 5°C . contains 2'1 per cent.(b) Saturated solution at 0°C . contains 1'6 per cent.

The Photogram.—We have received from the Editors of the *Photogram* a set of cards containing handy memoranda, chiefly upon photographic matters, including guide to correct exposure, rules for telephoto lens, how to find due south without a compass, photographic temperatures, cultivation of stereoscopic vision, &c. The cards are of a convenient size to fit the pocket-book, and the set can be obtained by applying to the office of the *Photogram*, London.

THE PASTY CONDITION ASSUMED BY ALUMINIUM NEAR ITS POINT OF FUSION, AND THE APPLICATION OF THIS PROPERTY TO THE CUTTING OF THE METAL.

By ALBERT GRANGER.

At the ordinary temperature aluminium is a hard metal. When we wish to cut or divide it by means of the ordinary tools found in a laboratory, such as a saw or a pair of scissors, we encounter a considerable amount of difficulty owing to the toughness of the metal.

When heated to about 600° the metal undergoes a change of structure, and its properties of tenacity and hardness are modified considerably. It becomes granular, and in this condition it can be broken with ease; if the temperature be raised to a sufficiently high point the metal can be completely crushed; it has become quite pasty.

The observation of this phenomenon certainly ought to have been made in the early history of the metallurgy of this metal, but it is singular that no mention is made of it in any of the books dealing with the physical properties of the metal, at least in none that I have come across. My reason for drawing attention to this interesting property, that is met with to a more or less developed extent in other metals, is that it is susceptible of practical application.

Aluminium is often met with commercially in sheets of such a size as to prevent their introduction into the ordinary glass vessels used in laboratories.

These sheets can be cut up very easily, as small as may be wished, by following the directions given below.

The piece of metal is heated (in a muffle furnace for preference) until it is at a dull red heat. From this point onwards aluminium offers much less resistance than at the ordinary temperature. The temperature is allowed to rise until the aluminium can be cut with the blade of an ordinary knife by exerting a little pressure. It can then be cut in strips or slices. The cut surface has a granular appearance, more favourable to attack by reagents than the usual smooth surface it has when cold. By using small quantities at a time it can be powdered in a mortar like zinc. If too large a quantity is tried at a time, the grains become agglomerated owing to the pressure of the pestle.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 15.

Manganate and Manganite of Barium.—G. Kassner and H. Keller.—The preparation of manganate of potash cannot be carried out easily or with advantage if we adhere to the conditions demanded by the equation given by Jolles:— $2\text{KMnO}_4 + 2\text{KOH} = \text{H}_2\text{O} + 2\text{K}_2\text{MnO}_4 + \text{O}$. A larger quantity of potash (KOH) is required, about one and a-half times to twice as much, to prevent the decomposition of the manganate formed. To obtain BaMnO_4 , we treat K_2MnO_4 with chloride of barium. The manganate of barium precipitated contains a little BaCO_3 , oxides of manganese, and always also a little permanganate which is formed towards the end of the reaction. The molecule of BaMnO_4 is not fixed to one molecule of water of crystallisation; by drying the salt *in vacuo*, the authors have been able, in fact, to reach such a point that it contained no more than 1'14 per cent of water, while the formula $\text{BaMnO}_4 \cdot \text{H}_2\text{O}$ requires 6'57 per cent. The reduction of the manganate to the condition of manganite is effected better by means of peroxide of hydrogen than by ferrocyanide of potassium. In fact, this latter salt easily leaves iron in the preparation; washings for the purpose of removing the metal dissociates the manganite into $\text{Ba}(\text{OH})_2$ and MnO_2 . The composition of the manganite corresponds to the formula $\text{BaMnO}_3 \cdot \text{H}_2\text{O}$; a desiccation lasting twelve weeks left 6'8 per cent of water in the salt, the preceding formula requiring 6'9 per cent.—*Arch. de Pharm.*, vol. ccxxxix., p. 473.

CONTRIBUTIONS TO OUR KNOWLEDGE OF
YTTERBIUM.*

By ASTRID CLEVE.

(Continued from p. 277).

III. COMPOUNDS OF YTTERBIUM (continued).

Ytterbium Selenates.

1. $\text{Yb}_2\cdot 3\text{SeO}_4 + 15\text{H}_2\text{O}$.

FROM very concentrated solutions a selenate separates out in the cold in small colourless scales, which probably contain the above amount of water, but possibly crystallise with $16\text{H}_2\text{O}$. At 110° the water passes off completely.

Analysis of the Pressed Substance.

0.8845 grm. of the substance suffered a loss in weight of 0.2276 grm. at 110° , and after strongly heating gave 0.3389 grm. of Yb_2O_3 .

		Calculated for $\text{Yb}_2\cdot 3\text{SeO}_4 + 15\text{H}_2\text{O}$, in per cent.		Found.
Yb_2O_3	..	394.2	37.69	37.19
3SeO_3	..	381.3	36.46	—
$15\text{H}_2\text{O}$	..	270.3	25.85	25.73
		1045.8	100.00	

2. $\text{Yb}_2\cdot 3\text{SeO}_4 + 8\text{H}_2\text{O}$.

Crystallises over the water-bath in large, transparent, hexagonal tables, which crumble quickly in the air. If a solution is cooled while crystallisation is taking place, the formation of this salt ceases, and instead the former salt is obtained, which is stable at lower temperatures.

Analysis of the Pressed Salt.

- 0.4618 grm. of the substance lost 0.0723 grm. at 110° , and on strongly heating gave 0.2020 grm. Yb_2O_3 .
- 1.3889 grm. (of another preparation) lost 0.2133 grm. at 120° , and on heating gave 0.5914 grm. Yb_2O_3 .

		Calculated for $\text{Yb}_2\cdot 3\text{SeO}_4 + 8\text{H}_2\text{O}$, in per cent.		Found.	
				I.	II.
Yb_2O_3	..	394.2	42.87	(43.73)	42.62
3SeO_3	..	381.3	41.46	—	—
$8\text{H}_2\text{O}$	..	144.16	15.67	15.66	15.43
		919.66	100.00		

The ytterbium result in Analysis I. is too high, probably owing to the difficulty of expelling the last traces of selenium from the oxide.

Specific Gravity and Molecular Volume.

- 1.4075 grm., specific gravity 3.46
- 1.4053 " " " " " " 3.52

Mean value 3.49
Molecular volume 263

3. Anhydrous Ytterbium Selenate, $\text{Yb}_2\cdot 3\text{SeO}_4$.

Results on heating either of the previous salts to $110-120^\circ$.

Specific Gravity and Molecular Volume.—0.8426 grm. Specific gravity, 4.14; molecular volume, 187.

Acid ytterbium selenite, $\text{Yb}_2\cdot 3\text{SeO}_3 + \text{H}_2\text{SeO}_3 + 4\text{H}_2\text{O}$, was prepared and analysed by Nilson (*loc. cit.*, p. 10).

Ytterbium Carbonates.

1. Neutral Ytterbium Carbonate, $\text{Yb}_2\cdot 3\text{CO}_3 + 4\text{H}_2\text{O}$.

Results as a colourless gelatinous precipitate on precipitation of a neutral solution of ytterbium nitrate with ammonium carbonate; after washing, it is free from ammonia.

Analysis of the Salt Dried in the Air.

- 0.7176 grm. of the substance gave up 0.0270 grm. of water over sulphuric acid, and at 100° 0.0538 grm. more. After precipitation with oxalic acid and ignition, 0.4771 grm. of Yb_2O_3 was obtained.
- 0.5270 grm. of the substance gave 0.3482 grm. Yb_2O_3 .

		Calculated for $\text{Yb}_2\cdot 3\text{CO}_3 + 4\text{H}_2\text{O}$, in per cent.		Found.	
				I.	II.
Yb_2O_3	..	394.2	65.89	65.80	66.08
3CO_2	..	132.	22.06	—	—
$4\text{H}_2\text{O}$	..	72.08	12.05	11.26	—
		598.28	100.00		

Three molecules of water were retained over sulphuric acid. In the salt thus dried the percentage of Yb_2O_3 found was 68.36 per cent (I.) and calculated for $\text{Yb}_2\cdot 3\text{CO}_3 + 3\text{H}_2\text{O}$ was 67.94 per cent.

Specific Gravity and Molecular Volume.

- 0.8794 grm. of the substance dried over sulphuric acid, specific gravity 3.676
- 1.0227 grm. of the substance dried over sulphuric acid, specific gravity 3.663

Mean value 3.670
Molecular volume 158

2. Basic Ytterbium Carbonate, $\text{YbOHCO}_3 + \text{H}_2\text{O}$
(Dried over Sulphuric Acid).

If carbon dioxide is passed for some time (about twenty-four hours) through freshly-precipitated ytterbium hydroxide suspended in water, the precipitate remains—as far as outward appearance is concerned—unchanged and gelatinous, and also after heating is quite amorphous, but has, as a matter of fact, been converted into the basic carbonate. At 100° the salt loses half the water, which is retained in the desiccator.

Analysis of the Salt Washed with Alcohol-ether and Dried over Sulphuric Acid.

- 0.5342 grm. of the substance gave, on heating in a combustion tube, 0.0541 grm. H_2O and 0.3914 grm. Yb_2O_3 .
- 0.5030 grm. of the substance lost at 100° 0.0283 grm. and gave 0.3676 grm. Yb_2O_3 .

		Calculated for $\text{YbOHCO}_3 + \text{H}_2\text{O}$, in per cent.		Found.	
				I.	II.
Yb_2O_3	..	394.2	73.51	73.77	73.04
2CO_2	..	88.	16.41	—	—
$3\text{H}_2\text{O}$	..	54.06	10.08	10.13	—
		536.26	100.00		

$1\frac{1}{2}\text{H}_2\text{O}$ 5.04 5.62 (loss of wt. at 100°).

In respect of the existence and method of preparation of the basic carbonate, ytterbium is allied to erbium and gadolinium, which both form under similar conditions salts of the same type (Cleve and Höglund, *Bull. Soc. Chim.*, 1872, xviii., 293; Benedicks, *Zeit. Anorg. Chem.*, xxii., 417). Samarium (Cleve, "Contributions to the Knowledge of Samarium," p. 23) and praseodymium hydroxides (v. Schéele, "Om Praseodym, &c.," *Inaug. Diss.*, Upsala, 1900, p. 66), on the other hand, take up CO_2 until neutral carbonates are formed.

On precipitating neutral ytterbium solutions with sodium carbonate, gelatinous precipitates are formed, which cannot be completely freed from sodium by washing. Up to the present it has not been definitely ascertained whether the retention of the sodium is due to the formation of a double salt, or to adhesion.

Ytterbium Borate, YbBO_3 .

Ytterbium oxide is only with difficulty attacked by boric anhydride when heated before the blowpipe.

* From the *Zeitschrift für Anorganische Chemie*, xxxii.

On heating for several hours with B_2O_3 in great excess, a fused mass is obtained, which, after being broken in pieces, is freed from unchanged boric anhydride by treating with dilute hydrochloric acid, ytterbium orthoborate being then left behind as a fine-grained crystalline sand. Since concentrated hydrochloric acid has no appreciable effect on the salt, for purposes of analysis it is evaporated with hydrofluoric acid, and the fluoride decomposed by means of sulphuric acid.

Analyses.

1. 1.0798 grm. of the substance in the coarsest possible crystals gave 1.4565 grm. $Yb_2 \cdot 3SO_4$.
2. 0.9440 grm. of the substance in fine crystals gave 1.2600 grm. $Yb_2 \cdot 3SO_4$.

Calculated for $YbBO_3$, in per cent.		Found.	
		I.	II.
Yb_2O_3 ..	394.2 84.92	85.77	84.87
B_2O_3 ..	70. 15.08	—	—
	464.2 100.00		

Cleve has prepared analogous ortho-borates of didymium and samarium.

Ytterbium Phosphates.

1. Ytterbium Ortho-phosphate, $YbPO_4 + 4\frac{1}{2}H_2O$.

From neutral solutions of the nitrate the ytterbium is completely precipitated by ordinary sodium phosphate (Na_2HPO_4). After washing, the gelatinous precipitate exhibits a neutral composition, while the filtrate and washings are rendered acid by phosphoric acid. Dried in the air, the phosphate thus obtained forms heavy semi-transparent particles, which give up some water over sulphuric acid, but even at 100° retain $2H_2O$.

Analyses of the Salt Dried in the Air.

1. 2.7426 grms. of the substance lost 0.3230 grm. in the desiccator; 1.4289 grms. of the residue gave up 0.0345 grm. of water at 100° .
2. 1.0302 grms. of the substance gave up 0.1334 grm. at 100° , and 0.0992 grm. more water before the blow-pipe.
3. 1.0602 grms. of the substance gave when fused with soda 0.3284 grm. $Mg_2P_2O_7$ and 0.5620 grm. Yb_2O_3 .
4. 0.5918 grm. of the substance gave 0.1956 grm. $Mg_2P_2O_7$.

Calculated for $YbPO_4 + 4\frac{1}{2}H_2O$, in per cent.		Found.			
		I.	II.	III.	IV.
Yb_2O_3 ..	394.2 56.44	—	—	55.91	—
P_2O_5 ..	142. 20.34	—	—	20.81	21.07
$4H_2O$..	72.08 10.32	—	9.63 (loss of weight above 100°).		
$5H_2O$..	90.10 12.90	13.89	12.95 (loss of weight at 100°).		
	698.38 100.00				

Although the results of the analyses do not agree very well with the theory,—as is scarcely to be expected in the case of amorphous precipitates such as this,—there can be no doubt concerning the neutral composition of this phosphate. Neutral ortho-phosphates of yttrium and erbium are similarly formed (Cleve; Cleve and Höglund).

2. Ytterbium Meta-phosphate, Yb_3PO_3 .

Attempts to prepare the phosphate $Yb_2O_3 \cdot 5P_2O_5$ according to the method described by Cleve, i.e., solution of the anhydrous sulphate in fused meta-phosphoric acid, led to the formation of the meta-phosphate Yb_3PO_3 , and not the desired compound. On boiling with water, the fused mass was for the most part dissolved. Only small quantities of a crystalline sand remained behind, and this was analysed.

1. 0.3287 grm. of the substance gave 0.2735 grm. $Mg_2P_2O_7$, and 0.1534 grm. Yb_2O_3 .
2. 0.2718 grm. of the substance (fresh preparation) gave 0.1316 grm. Yb_2O_3 .

Calculated for Yb_3PO_3 , in per cent.		Found.	
		I.	II.
Yb_2O_3 ..	394.2 48.03	46.67	48.42
$3P_2O_5$..	426. 51.97	53.06	
	820.2 100.00	99.73	

According to the analysis, some phosphoric acid was still mixed with Preparation 1.

The corresponding yttrium compound is known.

3. Ytterbium Phosphate, $Yb_2O_3 \cdot 2P_2O_5 + 5H_2O$.

In the preparation of the last salt most of the ytterbium went into the aqueous solution, as was pointed out. It was recovered from the solution, after strongly concentrating, as a gelatinous salt, $Yb_2O_3 \cdot 2P_2O_5$, but could not be separated directly by means of ammonia, probably owing to the formation of colloid soluble phosphates. After some time the solution becomes turbid, and the addition of ammonium chloride at once causes the formation of a precipitate, which again dissolves on washing.

When dried in the air, $Yb_2O_3 \cdot 2P_2O_5$ forms a heavy powder with 5 molecules of water, three of which are retained at 100° .

Analysis of the Salt Dried in Air.

- 0.3263 grm. of the substance lost 0.0181 grm. at 100° ; when heated before the blowpipe a further loss of 0.0226 occurred. 0.1854 grm. $Mg_2P_2O_7$ was obtained by the above method from the residue, and 0.1679 grm. Yb_2O_3 by precipitation with oxalic acid.

Calculated for $Yb_2O_3 \cdot 2P_2O_5 + 5H_2O$, in per cent.		Found.
Yb_2O_3 ..	394.2 51.30	51.46
$2P_2O_5$..	284. 36.97	36.22
$3H_2O$..	54.06 7.04	6.93 (loss of wt. above 100°)
$2H_2O$..	36.04 4.69	5.55 (loss of wt. at 100°)
	768.3	

Ytterbium Vanadates.

1. $3Yb_2O_3 \cdot 5V_2O_5 + 3H_2O$ (Dried at 100°).

Obtained as a yellow precipitate from ytterbium nitrate and ammonium vanadate.

Analysis.

- 0.5061 grm. of the substance dried at 100° gave, when dissolved in HCl and precipitated with oxalic acid, 0.2766 grm. Yb_2O_3 . By treating with nitric acid, 0.2158 grm. V_2O_5 was obtained from the filtrate.

Calculated for $3Yb_2O_3 \cdot 5V_2O_5 + 3H_2O$, in per cent.		Found.
$3Yb_2O_3$..	1182.6 55.04	54.65
$5V_2O_5$..	912. 42.45	42.64
$3H_2O$..	54.1 2.51	—
	2148.7 100.00	

2. $Yb_2O_3 \cdot 15V_2O_5$.

On concentrating the filtrate from the above insoluble vanadate over sulphuric acid, a brown crust was deposited which, on analysis, gave a considerably higher percentage of vanadium, although ytterbium nitrate was present in excess in the solution.

Analysis.

- 0.4112 grm. of the substance analysed as above gave 0.0530 grm. Yb_2O_3 and 0.3582 grm. V_2O_5 .

Calculated for $Yb_2O_3 \cdot 15V_2O_5$, in per cent.		Found.
Yb_2O_3 ..	394.2 12.55	12.89
$15V_2O_5$..	2536. 87.45	87.13
	2930.2 100.00	

Basic Potassium-ytterbium Chromate,
 $2\text{KYb}_2\text{CrO}_4 + \text{Yb}(\text{OH})_3 + 15\frac{1}{2}\text{H}_2\text{O}$.

If a neutral solution of ytterbium nitrate is mixed with neutral potassium chromate a yellow amorphous precipitate is formed, while potassium bichromate gives no precipitate.

The ytterbium salt must be present in excess in order that this double compound may be formed, otherwise the solution becomes yellowish red, and the precipitate then remains basic. As water causes decomposition, the salt is pressed directly for analysis without washing.

Analyses.

- 0.6831 grm. of the substance suffered a loss of weight of 0.1748 grm., equals 25.59 per cent at 100° . For $11\text{H}_2\text{O}$ the calculated loss is 24.93 per cent.
- 0.5055 grm. of the salt dried at 100° gave, on addition of HgNO_3 , 0.0658 grm. Cr_2O_3 . After the excess of mercury had been removed by means of sulphuretted hydrogen, 0.3142 grm. $\text{Cr}_2\text{O}_3 + \text{Yb}_2\text{O}_3$ was precipitated with ammonia; 0.2568 grm. of this precipitate was Yb_2O_3 . After the precipitate had been removed by filtration the solution gave 0.0360 grm. K_2O , weighed as KCl .

	Calculated for $2\text{KYb}_2\text{CrO}_4 + \text{Yb}(\text{OH})_3 + 4\frac{1}{2}\text{H}_2\text{O}$, in per cent.		Found.
$3\text{Yb}_2\text{O}_3$..	1182.6	49.52	50.74
$2\text{K}_2\text{O}$..	188.6	7.90	7.12
8CrO_3 ..	800.8	33.53	32.15
$12\text{H}_2\text{O}$..	216.24	9.05	—
	2388.24	100.00	

In preparing this substance, as was mentioned before, the ytterbium salt was present in excess, and as the salt was not washed, the K and Cr determinations are rather too low, and the Yb, on the other hand, somewhat high.

Ytterbium Molybdates.

1. $\text{Yb}_2\text{O}_3 \cdot 7\text{MoO}_3 + 6\text{H}_2\text{O}$ (Dried at 130°).

A solution of ytterbium nitrate, to which ammonium molybdate, $3(\text{H}_4\text{N})_2\text{O} \cdot 7\text{MoO}_3$, has been added in the cold, is not at once rendered turbid, but after some time the above salt separates out as a colourless opaque crust, which is insoluble even in hot water.

Analysis of the Salt Dried at 130° .

0.3692 grm. of the substance dissolved in nitric acid gave, on precipitation with ammonia, 0.1059 grm. Yb_2O_3 . 0.2608 grm. MoO_3 was separated from the filtrate by HgNO_3 .

	Calculated for $\text{Yb}_2\text{O}_3 \cdot 7\text{MoO}_3 + 6\text{H}_2\text{O}$, in per cent.		Found.
Yb_2O_3 ..	394.2	26.10	26.73
7MoO_3 ..	1008.	66.74	65.83
$6\text{H}_2\text{O}$..	108.17	7.16	—
	1510.37	100.00	

2. $2\text{Yb}_2\text{O}_3 \cdot \text{MoO}_3$.

If ytterbium earth is heated with excess of molybdenum trioxide in a flux of common salt, the earth is attacked only with very great difficulty, even when heated strongly before the blowpipe. The greater part remains undissolved, but it is finally converted into a heavy dark green crystalline powder.

Analysis.

0.7152 grm. of the substance gave, when treated with soda, 0.088 grm. MoO_3 and 0.6052 grm. Yb_2O_3 .

	Calculated for $2\text{Yb}_2\text{O}_3 \cdot \text{MoO}_3$, in per cent.		Found.
$2\text{Yb}_2\text{O}_3$..	..	84.56	84.62
MoO_3 ..	..	15.44	15.21
	100.00		99.83

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Wednesday, November 19, 1902.

Prof. J. EMERSON REYNOLDS, Sc.D., V.P.R.S., President,
in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Gilbert John Alderton, Eglington Road, Plumstead, S.E.; Harry Percy Lewis, Swansea Hematite Works, Landore; Thomas Samuel, School of Science and Art, Liscard, Cheshire; John Mello Wadmore, B.A., Meriden, Exmouth; Albert Wilmore, 158, Skipton Road, Colne; William Wade Yeomans, Middlewich, Cheshire.

The PRESIDENT announced that the Council that afternoon had appointed Dr. G. T. Morgan to be Editor of the publications of the Society from January 1st next.

Of the following papers, those marked * were read:—

*160. "The 'Dynamic Isomerism' of Thiourea and Ammonium Thiocyanate." By J. E. REYNOLDS, D.Sc., F.R.S., and E. A. WERNER, F.I.C.

The method of producing thiourea for use in the arts is still essentially that by which one of the authors succeeded in isolating the substance in 1868 (*Trans.*, vii., 1). This consists in carefully heating fused ammonium thiocyanate so as to secure as far as possible the molecular rearrangement represented by $\text{NH}_4\text{CNS} = \text{CSN}_2\text{H}_4$.

The proportion of thiourea actually formed at any single operation of this kind is known to be small. Volhard and others have variously estimated the yield at 15 to 22 per cent of the thiocyanate taken for conversion. It is also well known that pure thiourea, when melted, slowly reverts to ammonium thiocyanate; but the estimates of the extent of this reversion also vary considerably. Viewed as a "balanced action" conditioned by heat alone, these changes are cited by Lowry as examples of "dynamic isomerism."

In view of these discrepancies, which they considered were probably due to the use of small quantities of impure or moist materials, the authors have systematically studied on a comparatively large scale the effects of temperature and time on the course of these changes, and give the results of their experiments in curves. They show that:—

1. Ammonium thiocyanate fused, and then raised to, and maintained at, a steady temperature of 170° , underwent gradual change into thiourea until a maximum of 24.7 per cent was reached after forty-five minutes. Continued heating for twenty-five minutes longer led to slight loss of thiourea by decomposition.

2. In another series of experiments, the mean temperature being 182° , similar results were obtained, but the change was more rapid in the earlier stages, although the time required for the maximum effect was substantially the same as before.

3. Pure thiourea fused, and then maintained at a steady temperature of 170° , gradually reverted to ammonium thiocyanate, and after forty minutes only 25.8 per cent of thiourea remained. That proportion was not materially diminished by continued heating.

Therefore equilibrium is reached from either side when the isomerides are present in the melt in proportions which are substantially 25 per cent of thiourea and 75 per cent of ammonium thiocyanate, which is the composition of a definite compound having the formula $\text{CSN}_2\text{H}_4 \cdot (\text{NH}_4\text{CNS})_3$.

The authors conclude that the arrest of change is due to the production of this compound, which appears to be more stable at high temperatures than either of its constituents.

In confirmation of this view, they find that crystalline aggregates of nearly the above composition can be separated from the centre of a slowly cooled mass, produced by heating about a kilogram. of ammonium thiocyanate to 170° for forty minutes.

Further, having noted that the material which contained about 25 per cent of thiourea remained liquid down to 106° , they determined the points of complete liquefaction of a number of very intimate mixtures of pure thiourea and thiocyanate. They found that there was a regular decrease in melting-point from 148° (that of pure thiocyanate) to 106° , at which latter temperature a mixture containing 25 per cent of thiourea fused, but with still higher percentages of thiourea there was a regular rise in melting-point, as shown on a curve of eutectic form having its minor-point at 106° .

Finally, it was pointed out that the dissociation of the high temperature compound by solvents is by no means complete unless the latter are used in comparatively large proportions. Thus, when the melt was treated with insufficient warm acetone to dissolve it wholly, the solution afforded a compound which afterwards separated in feathery groups of crystals. This substance proved on analysis to be $CSN_2H_4 \cdot NH_4CNS$. With alcohol and water, the process of breaking down proceeds farther, but even warm water, if used in small proportion, does not cause complete separation, as fine, long crystals were easily obtained from such a solution which consisted of $(CSN_2H_4)_3 \cdot NH_4CNS$.

This compound is obviously complementary in composition to that which is formed in the fused mass at 170° . Re-solution of the crystals in water leads to complete separation.

Generally, the authors conclude that the state of equilibrium reached when either isomeride is heated to 170° for forty minutes is conditioned as much by perfectly definite chemical attraction as by heat.

*161. "Isomeric Partially Racemic Salts containing Quinquevalent Nitrogen. Part VIII. Resolution of the Hydrindamine Bromocamphorsulphonates." By F. S. KIPPING.

In previous communications (*Trans.*, 1900, lxxvii., 861; 1901, lxxix., 430), the author has described several cases of a new type of isomerism observed in the study of salts of *dl*-hydrindamine (and of *dl*-benzylhydrindamine) with bromo- and chloro-camphorsulphonic acids and with *cis*- π -camphanic acid; in order to account for the existence of these isomerides, it was assumed that each of the optically active bases gives rise to two salts, and that the four compounds thus formed unite in pairs to produce the two partially racemic isomerides.

Further investigation, which so far has been restricted to the isomeric hydrindamine bromocamphorsulphonates (distinguished as the " α "- and " β "-salts), seems to show that this view of their nature is substantially correct.

Resolution of the α -Salt.—When the α -salt (m. p. 150°), which separates unchanged from most ordinary solvents, is heated with a little ethyl acetate under suitable conditions, it is resolved into two components, one of which is deposited from the hot solution, whilst the other can be isolated from the mother-liquors. The former, provisionally called the αA -salt, crystallises in needles melting at about 223° ; the latter, the αB -salt, crystallises in needles melting at about 130° .

These two salts have practically the same specific rotation in dilute aqueous solution, namely, $[\alpha]_D = +60^\circ$; the molecular rotation, therefore, in both cases is $+266^\circ$, a value identical with that of bromocamphorsulphonic acid. The two compounds represent, nevertheless, salts of the enantiomorphously related hydrindamines, the bases having such low molecular rotations that they show no appreciable activity, even in moderately concentrated solutions of their hydrochlorides. The hydrochlorides, prepared from the αA - and αB -salts, are identical in ordinary properties, but the salts obtained by combining the bases from αA and αB with optically active acids are different; it follows, therefore, that the enantiomorphously related bases do not undergo racemisation when liberated from their salts.

Resolution of the β -Salt.—The partially racemic β -salt (m. p. 130°) is also resolved into different components

when it is crystallised from hot ethyl acetate under suitable conditions. The salt, which separates from the hot solution, crystallises in needles which appear homogeneous and which resemble αA very closely in outward and in optical properties; when, however, this compound is systematically crystallised from water, after some 30–40 operations, it is further resolved into a salt identical with αA and a new isomeride βA ; the latter is very similar to αA , but melts at a lower temperature (about 215°), and has a lower specific rotation ($[\alpha]_D = +56^\circ$) in aqueous solution; it is possible that this salt may not have been obtained quite free from αA .

The ethyl acetate mother-liquors, from which αA and βA have been deposited, contain unchanged β -salt together with two isomerides; one of these is identical with αB , but the other, βB , although very similar to αB in some properties, can be separated from it by fractional crystallisation from water. This fourth isomeride, βB , melts at about 130° , and has a specific rotation $[\alpha]_D = +39.5^\circ$ in aqueous solution.

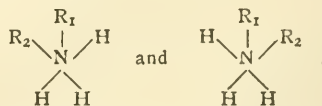
Synthesis of the α - and β -Salts.—When equal quantities of αA and αB are dissolved together in hot water, the solution deposits the partially racemic α -salt, and fractional crystallisation fails to reveal the presence of any β -salt in the product.

When αA and αB are separately decomposed with baryta, and the liberated bases are neutralised with the bromo-acid, the salts obtained appear to be identical with αA and αB respectively, but they are not so; for if now mixed in equal quantities and crystallised from water, they give a product which consists of a mixture of the α - and β -partially racemic salts. This is because, on uniting with the acid, the one base gives αA and βA , the other αB and βB ; the salt produced by combining the base from αB with the acid may, in fact, be resolved into αB and βB by fractional crystallisation.

When equal quantities of βA and βB are dissolved together in water, there results a salt which crystallises in hydrated prisms, indistinguishable in appearance from those of the partially racemic β -salt (m. p. 130°), but which, when dehydrated, melts at about 165° ; this fact, and the constant occurrence of four compounds in the products of the resolution of samples of the β -salt which have been repeatedly crystallised to free them from α -salt, show that the β -salt is composed of four isomerides. The salt composed of equal quantities of βA and βB seems to represent a new isomeride, in which case there would be three partially racemic salts.

*162. "Isomeric Compounds of the Type $NR_1R_2H_3$." By F. S. KIPPING.

From the results summarised in the preceding note, it will be seen that six isomeric salts have now been isolated from the mixture produced by the combination of *dl*-hydrindamine and *d*-bromocamphorsulphonic acid. Four of these salts, αA , αB , βA , and βB contain one molecule of one of the enantiomorphously related bases combined with one molecule of the acid; that is to say, each of the bases gives rise to two isomerides which may be represented by the symbols:—



Such compounds containing only three different radicles united with quinquevalent nitrogen, afford an example of a type of isomerism hitherto unknown; it is possible, however, that the isomerism of the optically inactive compounds of the type $NR_1R_2R_3R_4R_5$, described by Wedekind, may be of an analogous character.

The existence of these new isomerides has no doubt an important bearing on the question of the arrangement in space of the groups around a quinquevalent atom, and would seem to exclude the double tetrahedron configuration; also the view, very generally held, that the negative

ion in an ammonium salt takes up one particular valency. The fact that, in the case examined, the two radicles, R_1 and R_2 , are enantiomorphous does not of course preclude the possibility of the existence of isomerides in which the three different radicles are all optically inactive, and it may even be possible that an apparently simple salt, such as ammonium chloride, is in reality a mixture of two isomerides.

One particularly striking fact in connection with the isomeric hydrindamine salts is their stability; all the four simple isomerides have been repeatedly crystallised from boiling water and other solvents, and hitherto the conversion of one into the other has never been observed.

It is also interesting to note the highly abnormal molecular rotation of the $\beta\beta$ -isomeride; in 2 per cent aqueous solution, $[M]_D = +175^\circ$, whereas that of the acid is $[M]_D = +270^\circ$. Since the ordinary base ion, although enantiomorphous, has only an extremely low molecular rotation, it might be inferred that the $\beta\beta$ -isomeride is only very partially dissociated, and that there are two distinct types of ammonium salts.

*163. "The Oxime of Mesoxamide and some Allied Compounds. Part II. Disubstituted Derivatives." By Miss M. A. WHITELEY, D.Sc.

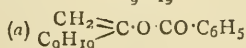
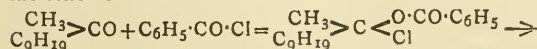
The following mono- and di-substituted derivatives of the oxime of mesoxamide have been prepared:—*Isonitrosomalondimethylamide*, m. p. 157° , the potassium and ferrous salts; *isonitrosomalonanilide*, m. p. 141° , the potassium, ferrous, and silver salts; *isonitrosomalondi-p-tolylamide*, m. p. $170-171^\circ$, the potassium and silver salts; *isonitrosomalonmono-p-tolylamide*, m. p. 183° ; *isonitrosomalondi-o-tolylamide*, m. p. 111° , the potassium salt; *ethyl isonitrosomalon-o-tolylamide*, m. p. $140-141^\circ$; *isonitrosomalondi-a-naphthylamide*, m. p. 184° , the potassium salt; *isonitrosomalondi- β -naphthylamide*, m. p. 221° , the acetyl derivative, m. p. 179° , a chlorinated derivative, m. p. 202° .

All these compounds possess the characteristic salt-forming properties exhibited by the original oxime, the alkali salts being yellow and the ferrous salts purple or blue. An interesting tautomerism is exhibited by some of them, the two isomerides differing from one another in colour (one being yellow and the other colourless), crystalline form, and solubility. The most probable explanation of this tautomerism is the assumption that the colourless isomeride has the *isoximino*-structure, whilst the yellow isomeride and the yellow salts correspond to the *oximino*-compound.

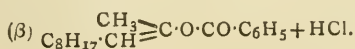
The examination of a fairly extensive series of α -oximino-ketones has shown that in addition to the well-known characteristic yellow colouration with alkalis, almost all give a deep purple or blue colour on the further addition of ferrous sulphate. This latter characteristic, however, appears to be influenced by the isomerism of the oximino-group, for α -benzil monoxime gives the reaction, whilst the β -isomeride does not. Again, among the dioximes, a considerable number, including α -benzil dioxime, were found to give a deep purple or brown colouration with ferrous sulphate and an alkali, whilst β - and γ -benzil dioxime gave no colouration under these conditions.

*164. "Interaction of Ketones and Aldehydes with Acid Chlorides—the Formation of Benzoxylefines and 1-Benzoxycamphene." By F. H. LEES.

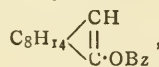
The author has found that methyl *n*-nonylketone and benzoyl chloride readily interact when boiled together, forming β -benzoxynonylene (α or β), $\text{CH}_2\text{:C(Obz)\cdot C}_9\text{H}_{19}$ or $\text{CH}_3\text{:C(Obz)\cdot CH\cdot C}_8\text{H}_{17}$. It is an oil, b. p. $233-235^\circ$ (50 m.m.), and is regarded as being formed according to the scheme—



or—

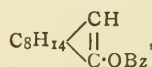


This formation of β -benzoxynonylene represents the first instance of the direct transformation of a mono-oxygenated ketone into a derivative of its enolic form. The author has extended this reaction to other ketones, an aldehyde, and an aliphatic acid chloride, the following substances resulting:— β -Benzoxynonylene (α or β), $\text{CH}_2\text{:C(Obz)\cdot C}_7\text{H}_{15}$ or $\text{CH}_3\text{:C(Obz)\cdot CH\cdot C}_6\text{H}_{13}$, from methyl *n*-heptylketone and benzoyl chloride, b. p. $210-211^\circ$ (50 m.m.); β -benzoxo- γ -methylheptylene (α or β), $\text{CH}_2\text{:C(Obz)\cdot CH(CH}_3\text{)\cdot C}_4\text{H}_9$ or $\text{CH}_3\text{:C(Obz)\cdot C(CH}_3\text{)\cdot C}_4\text{H}_9$, from methyl *sec*-hexylketone and benzoyl chloride, b. p. $197-200^\circ$ (50 m.m.); β -benzoxohexylene (α or β), $\text{CH}_2\text{:C(Obz)\cdot C}_4\text{H}_9$ or $\text{CH}_3\text{:C(Obz)\cdot CH\cdot C}_3\text{H}_7$, from methyl *n*-butylketone and benzoyl chloride, b. p. $170-175^\circ$ (50 m.m.); α -benzoxo- α -phenylethylene, $\text{C}_6\text{H}_5\text{:C(Obz)\cdot CH}_2$, from acetophenone and benzoyl chloride, b. p. $227-230^\circ$ (50 m.m.); 1-benzoxycamphene,—



from camphor and benzoyl chloride, b. p. $215-220^\circ$ (50 m.m.); α -benzoxo- α -heptylene, $\text{C}_5\text{H}_{11}\text{:CH\cdot CH(Obz)}$, from cinnamaldehyde and benzoyl chloride, b. p. 195° (50 m.m.); β -valeroxynonylene (α or β), $\text{CH}_2\text{:C(O\cdot CO\cdot C}_4\text{H}_9\text{)\cdot C}_9\text{H}_{19}$ or $\text{CH}_3\text{:C(O\cdot CO\cdot C}_4\text{H}_9\text{)\cdot CH\cdot C}_8\text{H}_{17}$, from methyl *n*-nonylketone and valeryl chloride, b. p. $185-190^\circ$ (50 m.m.).

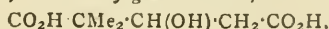
Acetone with benzoyl chloride, and methyl nonylketone with acetyl chloride, did not interact; methyl *n*-propylketone and benzoyl chloride interacted only slightly. All the substances prepared are nearly colourless and odourless oils, and in their chemical properties exactly resemble each other. They all readily absorb bromine, forming dibromo-addition products, and are unstable to potassium permanganate. The possibility of benzoxycamphene having a structure analogous to hydroxycamphene (Forster, *Trans.*, 1902, lxxxi., 264) was considered, but the fact that benzoxycamphene is readily hydrolysed by alcoholic hydroxylamine, yielding *l*-rotatory camphor-oxime, and that its dibromo-addition product readily splits up into α -bromocamphor and benzoyl bromide, definitely proves the correctness of the structure—



165. "The Synthesis of $\alpha\alpha$ -Dimethylglutaric Acid, of β -Hydroxy- $\alpha\alpha$ -dimethylglutaric Acid, and of the *cis*- and *trans*-Modifications of $\alpha\alpha$ -Dimethylglutaconic Acid." By W. H. PERKIN, jun., and Miss A. E. SMITH.

When a mixture of ethyl dimethylmalonate and ethyl acetate is treated with sodium, condensation readily takes place with the formation of ethyl $\alpha\alpha$ -dimethylacetonedicarboxylate, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which distils at $185-190^\circ$ (100 m.m.), and gives, in alcoholic solution with ferric chloride, a red-violet colouration. When this ester is reduced with sodium amalgam and then with hydriodic acid, it yields the following acids:—

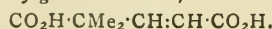
β -Hydroxy- $\alpha\alpha$ -dimethylglutaric acid,—



which crystallises from water in prisms, and melts at $158-160^\circ$.

$\alpha\alpha$ -Dimethylglutaric acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which melts at 90° , and is identical with the acid of this constitution obtained from isolauronic acid by oxidation with nitric acid.

cis- $\alpha\alpha_1$ -Dimethylglutaconic acid,—



This acid is readily soluble in water, and melts at 134° ; it combines with bromine, yielding *cis*- $\alpha_1\beta$ -dibromo- $\alpha\alpha$ -dimethylglutaric acid (m. p. 150°). When hydroxydimethylglutaric acid is distilled, it is, in part, converted into the sparingly soluble *trans*- $\alpha\alpha_1$ -dimethylglutaconic acid which melts at 172° , and was first obtained (Perkin, *Trans.*, 1902, lxxxi., 253) by the hydrolysis of ethyl α_1 -bromo- $\alpha\alpha$ -

dimethylglutarate, $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et}$, with alcoholic potash. This same acid is obtained almost quantitatively from the above hydroxy-acid by treatment with phosphorus pentachloride, then with alcohol, and finally with alcoholic potash,—



giving $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$. The *trans*-acid is acted on only with difficulty by bromine with formation of *trans*- α - β -dibromo-*aa*-dimethylglutaric acid (m. p. 217°). It appears, therefore, that the *cis*- and *trans*-modifications of *aa*-dimethylglutaconic acid melt respectively at 134° and 172°. The bearing of this on the work of Conrad and of Henrich on this subject was discussed.

166. "A Reaction of some Phenolic Colouring Matters."

II. By A. G. PERKIN and C. R. WILSON.

By means of alcoholic potassium acetate, gallacetophenone gives the salts (a) $\text{C}_8\text{H}_7\text{O}_3\text{K}\cdot\text{H}_2\text{O}$, and (b) $\text{C}_{24}\text{H}_{23}\text{O}_{12}\text{K}$. The former, pale yellow needles, identical with the compound which Nencki and Sieber (*Journ. Prakt. Chem.*, [2], xliii., 23, 546) prepared with alcoholic potash, is anhydrous at 160°, and gives the salt $\text{C}_{16}\text{H}_{14}\text{O}_8\text{Ba}$, yellow needles. Sodium acetate gives the salt $\text{C}_8\text{H}_7\text{O}_3\text{Na}\cdot\text{H}_2\text{O}$. With methyl iodide this gives gallacetophenonemethyl ether, $\text{C}_8\text{H}_7\text{O}_3(\text{OCH}_3)$, needles, m. p. 132–133°, the diacetyl derivative of which melts at 146–148°; and on methylation gallacetophenonedimethyl ether, m. p. 77–78° (*Trans.*, 1895, lxvii., 997), is formed. It is thus a para- or meta-methoxy-compound. The salt (b), colourless needles, is also formed from gallacetophenone and potassium acetate in aqueous solution, and from this the compound $\text{C}_{48}\text{H}_{46}\text{O}_{24}\text{Ba}$ can be obtained.

The following salts have been prepared with alcoholic potassium acetate. Ellagic acid gives $\text{C}_{14}\text{H}_5\text{O}_8\text{K}$ and $\text{C}_{14}\text{H}_4\text{O}_8\text{K}_2$, daphnetin, $\text{C}_9\text{H}_6\text{O}_4\cdot\text{KC}_2\text{H}_3\text{O}_2$, galangin, $\text{C}_{15}\text{H}_9\text{O}_5\text{K}\cdot\text{H}_2\text{O}$, kampheride, $\text{C}_{16}\text{H}_{11}\text{O}_6\text{K}\cdot\text{H}_2\text{O}$, dihydroxybenzalcumaranone ($\text{OH}:\text{OH}=6:7$), $\text{C}_{15}\text{H}_{10}\text{O}_4\cdot\text{KC}_2\text{H}_3\text{O}_2$, carminic acid, $\text{C}_{11}\text{H}_{11}\text{O}_6\text{K}$ and $\text{C}_{22}\text{H}_{22}\text{O}_{12}\text{Ba}$, styrogallol, $\text{C}_{16}\text{H}_7\text{O}_5\text{K}$, naphthazarine, $(\text{C}_{10}\text{H}_6\text{O}_4)_2\cdot\text{KC}_2\text{H}_3\text{O}_2$?, and curcumin, $\text{C}_{21}\text{H}_{19}\text{O}_6\text{K}$. By means of alcoholic potash daphnetin gives the salts $\text{C}_{18}\text{H}_{11}\text{O}_8\text{K}$ and $\text{C}_9\text{H}_5\text{O}_4\text{K}$, and carminic acid the salt $\text{C}_{22}\text{H}_{23}\text{O}_{12}\text{K}$. From acetyl rhamnetin, the compound $\text{C}_{16}\text{H}_{11}\text{O}_7\text{K}$ was obtained.

Dimethoxyanhydroglycogallol, $\text{C}_{10}\text{H}_{10}\text{O}_4$, yellow needles, m. p. 122°, gives with protocatechuic aldehyde dimethoxydihydroxybenzalcumaranone, $\text{C}_{17}\text{H}_{14}\text{O}_6$, orange-coloured needles, which with potassium acetate gives the salt $\text{C}_{17}\text{H}_{13}\text{O}_6\text{K}$. Pyrogallolmonomethyl ether, incidentally prepared, melts at 102–104°, and not at 95° as given by Benedikt (*Ber.*, 1877, ix., 125).

167. "Note on Mixtures of Constant Boiling-point."

By S. YOUNG, D.Sc., F.R.S.

It was noticed by Thorpe (*Trans.*, 1879, xxxv., 544) that when a mixture of equal volumes of carbon tetrachloride and methyl alcohol is distilled, a mixture of minimum boiling-point 55.6–55.9° comes over first. The vapour density of this distillate was found to be 41.82, and the composition was therefore:—

Carbon tetrachloride	..	..	..	..	78.1
Methyl alcohol	..	..	..	..	21.9
					100.0

At Dr. Thorpe's suggestion the author has determined the composition of the mixture of minimum boiling-point by the distillation method, and also from the specific gravity of the mixture after re-distillation.

The results are as follows:—

Distillation Method.

	From excess of CH_3OH .	From excess of CCl_4 .	From specific gravity.
CCl_4	79.99	79.35	79.44
CH_3OH	20.01	20.65	20.56
	100.0	100.0	100.0

The separation of the mixture of minimum boiling-point from methyl alcohol is very much more difficult than from carbon tetrachloride, and it is in all probability for this reason that the percentage of alcohol in Thorpe's distillate was too high, whilst that calculated from the results of the distillation of a mixture containing excess of alcohol was too low. The most accurate value is probably that deduced from the specific gravity of the re-distilled mixture of constant boiling-point.

Determinations by Thayer (*Journ. Phys. Chem.*, 1898, ii., 382), Ryland (*Amer. Chem. Journ.*, 1899, xxii., 384), and Carveth (*Journ. Phys. Chem.*, 1902, vi., 248) of the boiling-points and composition of mixtures of benzene with ethyl and methyl alcohol were compared with those of Miss Forster and the author (*Trans.*, 1902, lxxxi., 739).

168. "The Vapour Pressures and Boiling-points of Mixed Liquids." Part II. By S. YOUNG, D.Sc., F.R.S., and Miss E. C. FORSTER, B.Sc.

In a previous paper (*Trans.*, 1902, lxxxi., 752) it was shown that, so far as mixtures of chlorobenzene and bromobenzene are concerned, the conclusion of van der Waals is true that if the critical pressures of the two liquids are equal, and if the relation suggested by Galitzine and by Berthelot, $a_{12} = \sqrt{a_1 a_2}$ holds good, the relation between vapour pressure and molecular composition should be represented by a straight line, or the vapour pressures of mixtures may be expressed by the formula—

$$P = \frac{pP_A + (100 - p)P_B}{100}$$

where P, P_A , and P_B are the vapour pressures of the mixture and of the two components A and B at the same temperature, and p is the molecular percentage of A.

It does not, however, follow that it is only when the critical pressures are equal that the vapour pressures agree with the formula; indeed, Speyers goes so far as to state that it is always applicable to mixtures of liquids of normal molecular weight.

As the statement of Speyers is certainly too general, it seemed desirable to determine the boiling-points of mixtures of a number of closely related compounds the critical pressures of which are not equal.

Four pairs of such liquids were examined, (1) ethyl acetate and ethyl propionate, (2) toluene and ethyl benzene, (3) *n*-hexane and *n*-octane, (4) benzene and toluene, and, in addition, carbon tetrachloride and benzene.

The investigation resulted in the following conclusions:—

1. The volume and temperature changes on mixing closely related substances are in all the observed cases very small, but it is only with chlorobenzene and bromobenzene that they can certainly be said to be within the limits of experimental error. With the two esters these limits are very closely approached, whilst with benzene and toluene, which are somewhat less closely related, the changes are distinctly larger, and for mixtures of benzene with *n*-hexane and with carbon tetrachloride they are very much larger.

2. The formula—

$$P = \frac{pP_A + (100 - p)P_B}{100}$$

is nearly, if not quite, true for closely related liquids, even when the critical pressures are widely different; it is not true, however, as a rule, for mixtures of liquids of normal molecular weight, such as benzene and *n*-hexane, or for benzene and carbon tetrachloride which are not closely related.

Of the five pairs of closely related liquids examined, it is only chlorobenzene and bromobenzene which show absolutely no temperature or volume change on mixing, and for mixtures of which the vapour pressures are accurately given by the above formula, and it is only this pair of liquids which have the same critical pressure. The deviations in the other cases are, however, so small that

it remains an open question whether equality of critical pressure is a necessary criterion for absolute agreement with the formula. It appears, at any rate, that equality of critical pressure without closeness of chemical relationship is not a sufficient criterion.

It may be stated definitely that in the case of closely related substances, whatever their critical pressures, the deviations are, as a rule at any rate, exceedingly small.

Lastly, it is shown that there is strong evidence for the existence of mixtures of minimum boiling-point in the case of carbon tetrachloride and benzene, and also of *n*-hexane and benzene, although the boiling-points of the mixtures could hardly be distinguished from those of carbon tetrachloride and *n*-hexane respectively by ordinary thermometric methods.

169 "The Vapour Pressures and Boiling-points of Mixed Liquids." Part III. By S. YOUNG, D.Sc., F.R.S.

If the vapour pressures of mixtures of two liquids, A and B, are accurately expressed by the formula—

$$P = \frac{pP_A + (100 - p)P_B}{100}$$

(where P , P_A , and P_B are the vapour pressures of the mixture and of the two components respectively at the same temperature, and p is the molecular percentage of A), and if the difference between P_A and P_B is small the relation between the boiling-points of the mixtures at constant pressure and their molecular composition is represented by a nearly straight line, and the temperature may with small error be calculated by means of the formula—

$$t = t_B + \frac{p}{100} (t_A - t_B).$$

The greater the difference between P_A and P_B , the greater is the deviation of the boiling-point composition curve from a straight line, and the higher is the molecular percentage of A in that mixture which shows the maximum deviation, D . This percentage is given with fair accuracy by the formula $p_D = 50 + 0.18\Delta$ (where Δ is the difference between the boiling-points of A and B), and the maximum deviation may be calculated with very slight error from the formula—

$$D_2 = - \frac{0.000158 \Delta^2}{c' \cdot T'} \cdot \frac{c_A}{c_B},$$

where c_A and c_B are the values of $\frac{dt}{dp} \cdot \frac{1}{T}$ for the two components—

$$c' = \frac{(50 + 0.18\Delta) c_A + (50 - 0.18\Delta) c_B}{100}$$

and—

$$T' = \frac{(50 + 0.18\Delta) T_A + (50 - 0.18\Delta) T_B}{100}.$$

The values of D_2 , calculated from the above formula, and of D_1 , deduced from the actual vapour pressures (*Trans.*, 1902, lxxxii., 752) for nineteen pairs of closely related compounds, were shown in a table. The greatest difference between D_2 and D_1 is 0.16° , although the actual value of D_1 is in one case -32.8° . The boiling-point curves have been determined experimentally in five cases, and the maximum deviation, D_3 , read from the curves; the greatest difference between D_3 and D_1 is 0.27° .

For mixtures of liquids which are not closely related, the formula—

$$P = \frac{pP_A + (100 - p)P_B}{100}$$

is not, as a rule, applicable, but if the ratio c_A/c_B lies between 0.95 and 1.05 (probably between 0.9 and 1.1), D_2 agrees well with D_1 , and in other cases the difference rarely amounts to one degree. The observed boiling-points of mixtures differ, however, as a rule, from those deduced from the vapour pressures, more especially when the molecules of one or both liquids are associated.

Whether a mixture of constant boiling-point can be

formed or not depends chiefly on the relative values of Δ and $D_3 - D_1$. If Δ is very small, such a mixture may be formed even when the difference between D_3 and D_1 is less than 1° , as in the case of carbon tetrachloride and benzene ($\Delta = 3.44^\circ$, $D_3 - D_1 = -0.89^\circ$). On the other hand, methyl alcohol and water do not form such a mixture, although $D_3 - D_1 = -4.95^\circ$, Δ having in this case the high value 35.11° .

170. "Note on the Condensation Points of the Thorium and Radium Emanations." By E. RUTHERFORD and F. SODDY.

It was shown (*Trans.*, 1902, lxxxii., 342) that the radioactive emanation from thorium compounds passed in unchanged amount through a tube cooled to -78° with solid carbon dioxide and ether. The acquisition of a liquid air plant has enabled the authors to repeat the experiment at a lower temperature, with the result that they have now succeeded in condensing both the thorium and the radium emanations.

A current of hydrogen (or of air) was passed through the thorium or radium compound, and thence through a copper spiral cooled in liquid air. No trace of emanation escaped in the issuing gas either in the case of radium or of thorium. At the temperature of liquid air the emanations are therefore either condensed or lose their activity.

The radium (or thorium) compound was then removed, and the gas current sent directly through the spiral tube, which was quickly taken out of the liquid air and placed in cotton-wool. Nothing happened for two or three minutes as the temperature of the spiral slowly rose, until suddenly the presence of the emanation was observed in large amount in the escaping gas. The result therefore cannot be explained by supposing that the emanations lose their ionising power at the temperature of liquid air. It is clear that they are condensed and again volatilised. From the sharpness and suddenness of the phenomena there appeared to exist for each emanation a definite temperature of volatilisation. This temperature is very nearly the same in the two cases and considerably above the boiling-point of liquid air.

By measuring the temperature of the copper spiral at the instant of volatilisation, it was found that successive determinations agreed amongst themselves to within a degree. The exact temperatures cannot yet be given, but as a first approximation it may be said that for the radium emanation the volatilisation point lies in the neighbourhood of -130° , and for the thorium emanation about five degrees lower.

This experiment furnishes an additional proof—if such were needed—that radio-activity is accompanied by the continuous production of special kinds of active matter, which possess distinct and sharply defined chemical and physical properties.

171. "Note on the Action of Barium Hydroxide on Dimethylvioluric Acid." By Miss M. A. WHITELEY, D.Sc.

When dimethylvioluric acid is decomposed by boiling with barium hydroxide, the chief product is isonitrosomalondimethylamide, which crystallises in well developed prisms belonging to the monosymmetric system ($a:b:c = 1.53394:1:0.88680$; $\beta = 68.43^\circ$); it melts at 157° , and yields a yellow potassium salt and a purple ferrous salt, both of which are crystalline. In addition to this compound, six other decomposition products can be isolated, one, melting at $239-240^\circ$, has not been identified, the other five are carbon dioxide, oxalic acid (as barium salts), monomethylloxamide, methylamine, and methylamine oxamate. Andreasch (*Monatsh.*, 1895, xvi., 17), who first examined this reaction, obtained only three products, namely, carbon dioxide, methylamine, and a crystalline compound melting at 228° , which he identified as isonitrosomalondimethylamide; this investigation, however, indicates that it was probably an impure specimen of monomethylloxamide.

172. "The Determination of Strychnine and Brucine in *Nux vomica*." By E. DOWZARD.

In order to determine the strychnine, the pure mixed alkaloids are dissolved in 50 c.c. of 2 per cent sulphuric acid, 5 c.c. of nitric acid are added, and the mixture allowed to stand fifteen minutes; the solution is transferred to a separator containing 15 c.c. of ammonia (sp. gr. 0.890) and 10 c.c. of chloroform; the mixture is shaken for five minutes, the solvent separated, and the alkaline liquid again shaken with 10 c.c. of chloroform. The mixed chloroform washings are now shaken with 15 c.c. of dilute ammonia (1 c.c. of above-mentioned strength diluted to 45 c.c.); this is repeated twice, the chloroform evaporated off, and the residue dried at 100° until constant.

To determine the brucine, a standard brucine solution is required, which is made by dissolving 0.16 gm. of anhydrous brucine and 0.16 gm. of strychnine in 2 per cent sulphuric acid, and the solution made up to 100 c.c. Then 0.10 gm. of the pure mixed alkaloids is dissolved in 50 c.c. of 2 per cent sulphuric acid; this solution and 50 c.c. of the standard are placed in two small beakers, 5 c.c. of nitric acid (sp. gr. 1.42) are added simultaneously to the contents of each beaker; the solutions are then transferred to the comparison troughs of a Gallenkamp colorimeter. Five minutes after adding the nitric acid, six readings are taken; from the average of these, the brucine is calculated.

Results were given which proved the accuracy of the determination made by both these methods.

PHYSICAL SOCIETY.

Ordinary Meeting, November 28th, 1902.

Prof. S. P. THOMPSON, President, in the Chair.

THE meeting was held, by invitation of Prof. Callendar, in the Physical Laboratory of the Royal College of Science.

Prof. PERRY read a paper on "A Slide-rule for Powers of Numbers."

Soon after the reading of Mr. Lanchester's paper in 1895, "The Radial Cursor; a New Addition to the Slide-Rule," Prof. Perry made slides to assist in computing m^n , where m and n are any numbers. He then came to the conclusion that no great accuracy was obtainable; but on trying the method again he has recently found that it is very convenient and sufficiently accurate for gas- and steam-engine work. These computations can be made with a table of values of $\log(\log n)$ used in conjunction with an ordinary table of logarithms. In the rule exhibited the D line is replaced by a scale such that the distance from the mark 10 to the mark m represents $\log(\log m)$ to the same scale of measurement as that to which the distance from 1 to n on the C scale represents $\log n$. The values of m range from 2 to 1000, and those of n from 1 to 10 or from 1 to 0.1 used backwards. The author showed how, with one operation, the rule could be

used to find the value of $\frac{a}{m^n}$, $\frac{1}{m^n}$, and the logarithm of any number to any base. If the answer on scale D is less than 2 or greater than 1000, or if the exponent n is negative, indirect methods involving two operations are necessary. Prof. Perry has replaced the ordinary D line by the log.log scale, because in his opinion this line is the one least used by workers with the slide-rule. The use of the log.log scale was described by Roget in 1814, and the author's object in bringing the matter forward lies in the fact that Dr. Roget's paper seems to be almost unknown, and it is only in these modern days that the computations for which he invented the rule have to be frequently made.

Mr. HARRISON said there could be no doubt that many who had to make calculations would avail themselves of the advantages offered by the addition of the log.log scale to the ordinary slide-rule. He would like to call attention to a further addition by which the general utility of the

log.log scale was increased. It was the introduction of a log. (-log) scale which increased the range of the instrument by making it possible to deal with numbers from a small fraction upwards, with the exception of an unavoidable gap near unity. It also made it possible to directly evaluate a quantity like a^{-n} . In a slide-rule, if the cursor were misplaced by a small amount, the consequent error in the reading of the log. scale was, for all positions, the same fraction of the number read. On the other hand, in the log.log scale the proportionate error varied along the scale, and was least at the unity end. At the particular place at which the reading is " e " or " $-e$ " the percentage error agreed with that of the comparison log scale. At any other place where the reading was e^n the error would be n times this amount. This proportionate accuracy was exactly that which was justified in dealing with experimental numbers liable to a percentage error. It was always possible to increase the degree of accuracy by splitting the numbers involved into suitable factors. Mr. Harrison also gave some account of the preparation of a ten-inch slide-rule accurate to one part in 300, which he hoped it would be possible to sell for one shilling.

Prof. EVERETT said that the slide-rule exhibited by Prof. Perry would be useful for people constantly engaged in raising numbers to strange indices. For occasional use he thought that a table of logarithms was preferable. He pointed out that a complete history of the slide-rule was given in the introduction to the original edition of Hutton's Tables. There were two distinct methods of using logarithmic scales—one due to Gunter and sensibly the same as that employed in Fuller's spiral rule, and the other that used in ordinary slide-rules. With his own form of rule, which he found very convenient, it was possible with care to work correctly to one part in four thousand.

Mr. BOYS remarked that the slide-rule had occupied his attention for many years. The device employed by the author for dealing with powers of numbers was perfectly well known, and the log.log scale was usually referred to as the P line. He admitted that the P line was not so much used as it should be, and hoped that the paper would serve a good purpose in drawing attention to it. He thought, however, that in working with gas- and steam-engines Lanchester's rule was eminently suitable for dealing with cases in which numbers had to be raised to fractional indices. He agreed with Mr. Harrison's remarks upon the accuracy of the exponential scale, but said that they were apt to create a wrong impression. In dealing with an experimental number subject to error the accuracy obtained by the scale was sufficient, but in raising a true number to a certain power the errors introduced were large. He disagreed with Prof. Perry in his assertion that the ordinary D line was less used than the others.

Prof. GREENHILL expressed his interest in the papers and the remarks of Mr. Boys. He thought it would be better to preserve the D line and replace the C line by the log.log scale. He also exhibited the form of Fuller's rule used by the R.H.A.

Mr. APPLEYARD referred to the advantages of the spiral form of slide-rule, and asked if it would be possible to design the sliding part of an ordinary rule on geometrical principles to get rid of the sticking, which frequently occurs.

Mr. COOPER supported Mr. Boys and Prof. Greenhill with reference to the D line, and said he thought it ought not to be abolished.

The CHAIRMAN said an exponential rule was a very useful thing in dealing with some of the calculations connected with alternating currents. A simple method for carrying out a lot of operations for which the slide-rule is often used, would be to commit to memory the multiplication table up to thirty-three times thirty-three.

Prof. H. L. CALLENDAR exhibited a Lecture Experiment for the Determination of the Mechanical Equivalent of Heat.

The experiment was carried out with a modified form of the apparatus exhibited and described by Prof. Callendar at the meeting of the Physical Society held on June 20th, 1902. In the original apparatus conduction from the calorimeter was prevented by ebonite bushes, and the stability of the motion was secured by using a compound belt of silk and leather. In the new pattern the calorimeter is much lighter, and is fastened to driving-cheeks by steel bolts and ivory distance-pieces. The increased conduction loss is compensated by the diminished air loss. Owing to the chemical action of leather on brass, the original belt was removed, and a belt of double and single silk ribbon substituted. A small spring-balance has been introduced to secure stability, and the difference of the weights at the ends of the belt can be read to an accuracy of one part in four thousand. In the actual experiment performed at the meeting, Count Rumford's compensation method was adopted to eliminate the errors arising from loss of heat by radiation and conduction, the calorimeter being half-filled with water at a suitable temperature less than that of the laboratory. The calorimeter was then made to revolve on a horizontal axis by means of an electric motor, and the air-temperature was determined with a platinum thermometer fixed near to the instrument. The experiment was performed by observing the temperature of the water in the calorimeter at a certain instant, and again after every successive 100 revolutions up to 600. The air-temperature was then re-determined, and the mean air-temperature during the experiment calculated. The interval selected for the calculation of J was from the first reading of the temperature of the calorimeter until the time when the mean temperature of the calorimeter throughout the experiment was the same as the mean temperature of the air. The initial and final air-temperatures were $19^{\circ}07$ and $19^{\circ}40$, giving a mean of $19^{\circ}24$. The temperature of the water in the calorimeter at the commencement of the observation was $16^{\circ}17$, after 500 revolutions it was $21^{\circ}59$, and after 600 revolutions $22^{\circ}59$. By interpolation it was found that the mean temperature of the calorimeter throughout the experiment was, after 558 revolutions, the same as the mean air-temperature. The rise of temperature was found to be $6^{\circ}00$, and the value of J deduced from the experiment was $4^{\circ}22$ joules per calorie.

Prof. EVERETT congratulated Prof. Callendar upon the success of the experiment.

The CHAIRMAN expressed his interest in the apparatus and the experiment, and said that a few years ago he would have been surprised at the possibility of determining J in ten minutes. He thought, however, it was more surprising that it was possible to determine in front of an audience temperatures to within $1/100^{\circ}$ C. This had been rendered possible by the introduction of the platinum thermometer, and he felt that Prof. Callendar had had a large share in bringing that instrument to its present state of perfection.

A paper on "*A Portable Capillary Electrometer*" was postponed until the next meeting.

The Society then adjourned until December 12th, 1902.

CORRESPONDENCE.

"FIXING" NITROGEN FROM THE ATMOSPHERE.

To the Editor of the Chemical News.

SIR,—The atmosphere covering a square mile of the earth's surface would furnish sufficient nitrogen for ten years' supply of sodium nitrate at the rate of 12 million tons of nitrate a year. To put it in another way—Had the fixation of nitrogen from the atmosphere by electrical synthesis and absorption with alkali been commenced some ninety years before the beginning of the Christian

Era and been continued up to the present time, with the same annual output of 12 million tons of sodium nitrate, the effect on the atmosphere would have been so slight as not to show itself by the ordinary methods of gas analysis. In fact, only a millionth of the available nitrogen would have been consumed!

Such a supposed slight deterioration of the atmosphere is, however, founded on an assumption which is more or less questionable, viz., that nitrogen once fixed never finds its way back into the atmosphere.

The same general conclusions apply to oxygen, so that I can scarcely agree with Mr. W. H. Deering in regarding the electrical process of producing nitrates as likely to be a serious draft on the atmosphere.—I am, &c.,

WM. ACKROYD.

Halifax, December 2, 1902.

THE SUPPOSED DISCOVERY OF ALUMINIUM TWO THOUSAND YEARS AGO.

To the Editor of the Chemical News.

SIR,—Can the quotation in your issue of October 3 (vol. lxxxvi., p. 171), regarding the supposed discovery of aluminium two thousand years ago, have reference to the following passage from Pliny's "*Natural History*," Book XXXVI., Chapter 26? I quote from the classic translation of Philemus Holland.

"Moreover, it is said, That during the reign of Tiberius the Emperor, there was devised a certain temper of glasse, which made it pliable and flexible to wind and turn without breaking: but the artificer who devised this, was put downe, and his work-house, for feare lest vessels made of such glasse should take away the credit from the rich plate of brasse, siluer, and gold, and make them of no price: and verily, this bruit hath run currant a long time (but how true, it is not so certain)."

I have not been able to find any other passage in Pliny which could have given rise to the quotation in the *Globe*. If, however, there be such a passage, the inference need not be drawn that aluminium was known to the ancients. Pliny has, indeed, summed up in his "*Natural History*" all the knowledge of a scientific character which was to be found in a very complete search of earlier authors, and he supplemented it from his own experience, but unfortunately he did not use any discriminating editorial criticism. The result is a most interesting jumble of science and myth, of fact and fancy, upon which little reliance can be placed.

It is to be hoped that some day a translation of the "*Natural History*" will be published edited by a competent scientific man.—I am, &c.,

JAS. LEWIS HOWE.

Washington and Lee University,
Lexington, Virginia, November 19, 1902.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

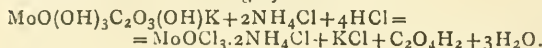
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 20, November 17, 1902.

Impurities of Compressed Oxygen and their Effect on Combustions in the Calorimetric Bomb.—M. Berthelot.—When oxygen is used in the calorimetric bomb for determining heats of combustion, it is essential that the gas should be free from all combustible matter. Water vapour and carbon dioxide (the latter in small traces) do not interfere with calorimetric measurements. In many cases it is advantageous to saturate the oxygen with water

vapour before the combustion, as it renders negligible the calorific effect due to reduction to vapour of the water produced by the combustion itself. Traces of nitrogen present in the oxygen cause nitric acid to be produced, and an error occurs in the result in consequence. The presence of hydrogen or combustible gases has also to be allowed for. It is necessary to make all junctions with metallic copper without using any organic materials. In one experiment it was found that the quantity of oxygen introduced into the bomb contained practically no carbon dioxide, but 0.0005 gm. of free hydrogen. This weight is susceptible of developing 17.2 cal. of heat during its combustion.

Atmospheric Hydrogen.—Anatole Leduc.—The author's experiments lead him to the conclusion that former researches on the proportion of hydrogen in the atmosphere cannot be correct.

The Oxalomolybdates.—M. Bailhache.—The author prepares complex oxalates from sulphate of molybdenum, $\text{Mo}_2\text{O}_3 \cdot 2\text{SO}_3$, and examines their reactions. If these react on sodium acetate in a current of hydrogen, a precipitate is formed. This, when washed with alcohol and dried, gives proportions of metal and oxygen which are not constant. This fact can be explained by the supposition that the salt is a variable mixture of hydrated molybdenum dioxide and another hydrate, $\text{Mo}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The reactions obtained by an aqueous solution of molybdenum sulphate confirm this theory. When ammonium chloride is added and the solution saturated with hydrochloric acid gas, green crystals of double chloride of molybdenyl and ammonium are deposited. Oxalomolybdate of potassium also gives this characteristic reaction when dissolved with ammonium chloride in strong hydrochloric acid—



MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter:—

Professor H. S. Hele-Shaw, Six Lectures (adapted to young people) on "Locomotion—on the Earth; through the Water; in the Air"; experimentally illustrated.

Professor Allan Macfadyen, Fullerian Professor of Physiology, R.I., Six Lectures on "The Physiology of Digestion."

Sir William Abney, Three Lectures on "Recent Advances in Photographic Science."

Sir Robert Ball, Three Lectures on "Great Problems in Astronomy."

Mr. A. J. Evans, Three Lectures on "Pre-Phœnician Writing in Crete, and its bearings on the History of the Alphabet."

Sir Clements Markham, Three Lectures on "Arctic and Antarctic Exploration."

Mr. G. R. M. Murray, Three Lectures on "The Flora of the Open Ocean."

Mr. C. H. Firth, Three Lectures on "Society during the Commonwealth and Protectorate."

Sir Frederick Bridge, Three Lectures on "The Bicentenary of Samuel Pepys—His Musical Contemporaries, Criticisms, and Compositions" (with Musical Illustrations).

Mr. A. B. Walkley, Three Lectures on "Dramatic Criticism."

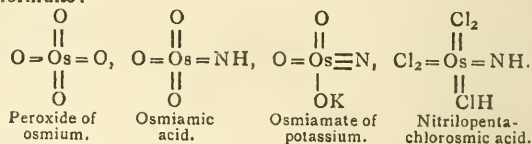
Six Lectures by The Right Hon. Lord Rayleigh.

The Lectures on Tuesdays and Thursdays during the Season 1903 will be delivered at Five o'clock instead of at Three, as in previous years. The Christmas Course of Juvenile Lectures and the Saturday Lectures will continue to be delivered at three o'clock.

The Friday Evening Meetings will begin on January 16th, when a Discourse will be delivered by Professor

Dewar on "Low Temperature Investigations"; succeeding Discourses will probably be given by Dr. Tempest Anderson, Professor W. E. Dalby, The Right Hon. Sir Herbert Maxwell, Bart., M.P., Professor S. Delépine, Principal E. H. Griffiths, Dr. A. Liebmam, Professor J. G. McKendrick, Professor Karl Pearson, Professor E. A. Schäfer, Professor W. A. Herdman, The Right Hon. Lord Rayleigh, and other gentlemen.

The Nitrilopentachlorosmiate, and on the Constitution of Osmiamic Acid.—A. Werner and K. Dinklage.—We treat 1 gm. of finely powdered osmiate of potassium with 4 c.c. of concentrated hydrochloric acid, cooling and stirring the whole time; chlorine is given off. After half-an-hour crusts of red crystals are deposited, which are purified by draining, re-dissolving in a little water, and re-precipitating with hydrochloric acid. In this manner we obtain a reddish brown crystalline powder, soluble in water, with a cherry-red colour, but decomposed, giving a brown precipitate, after prolonged contact with water. It is insoluble in the organic solvents; on boiling with potash there is no disengagement of ammonia. The formula of this body is OsNCl_5K_2 , and the authors call it *nitrilopentachlorosmiate of potassium*; the mother-liquors contain the corresponding free acid, OsNCl_5H_2 , and the reaction can be explained in the following manner by admitting that a monopotassic salt is formed first: $\text{OsNO}_3\text{K} + 7\text{HCl} = \text{OsNCl}_5\text{KH} + \text{Cl}_2 + 3\text{H}_2\text{O}$. The mother-liquors, treated with chloride of ammonium, precipitate a violet microcrystalline powder, which is the corresponding ammoniac salt, $\text{OsNCl}_5\text{H} \cdot \text{NH}_4$, similar to the potassic salt. In the same way we can get the salts of caesium and rubidium; they are still less soluble, especially the latter. The authors think that the osmium is octavalent, and propose the following constitutional formulæ:—



—*Berichte*, vol. xxxiv., p. 2698.

MEETINGS FOR THE WEEK.

MONDAY, 15th.—Society of Arts, 8. (Cantor Lectures). "The Future of Coal-gas and Allied Illuminants," by Prof. Vivian B. Lewes.

WEDNESDAY, 17th.—Chemical, 5.30. "A Reagent for the Identification of Carbamide and of certain other Nitrogen Compounds," by H. J. H. Fenton. "The Rate of Decomposition of Diazo-compounds—Part II. Diazo-compounds of the Naphthalene Series," by J. C. Cain and F. Nicoll. "The State of Carbon Dioxide in Aqueous Solution" and "Qualitative Separation of Arsenic, Antimony, and Tin," by J. Walker. "The Hydrates and Solubility of Barium Acetate," by J. Walker and W. A. Pyffe. "The γ -Dimethylglutaric Acids, and the Separation of *cis*- and *trans*-forms of Substituted Glutaric Acid," by J. F. Thorpe and W. J. Young.

Microscopical, 8. "The Genus *Diaschiza*," by F. R. Dixon-Nuttall and Rev. R. Freeman. Demonstration on a New Arrangement for taking Photomicrographs in Colours, by E. R. Turner.

Society of Arts, 8. "The South Russian Iron Industry," by Archibald P. Head, M.Inst.C.E.

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THE CHEMICAL NEWS.

VOL. LXXXVI., No. 2247.

SOME REMARKS ON THE CONNECTION BETWEEN METALS AND NON-METALS.

By GEOFFREY MARTIN, B.Sc.(Lond.).

A GENERAL study of the Periodic Table shows that in any one group an increase of atomic weight almost invariably causes metallic properties to appear. This is well seen in the case of the group elements, C, Si, Ge, Sn, Pb, of Group IV., and N, P, As, Sb, Bi, of Group V.

In each case it seems that there is a gradual transition, with increase of atomic weight, of the non-metals into metals. The same relationship holds in almost all the other groups.

Now, it is a very remarkable fact that, in the case of the elements of the odd series at any rate, when an increase of atomic weight brings out metallic properties, it produces also at the same time a similar effect on the chemical behaviour of the elements as an increase of temperature.

To illustrate this, let us take the case of the elements C, Si, Ge, Sn, and Pb.

Carbon and silicon at ordinary temperatures are very stable in a tetravalent condition, and extremely unstable in a divalent state. But as the atomic weight increases, the divalent condition becomes more and more stable, and the tetravalent condition more and more unstable, until finally, in the case of lead, the divalent condition is far more stable than the tetravalent condition, as appears at once manifest on contrasting PbCl_4 with PbCl_2 , and PbO_2 with PbO .

Now, this is precisely the same effect as an increase of temperature alone would bring about. Almost invariably the higher the temperature the more and more do elements tend to pass from a higher to a lower grade of valency.

Iron, for example, at ordinary temperatures is very stable in the Fe^{III} state, and unstable in the Fe^{II} state, as at once appears when we contrast FeCl_3 with FeCl_2 . But at a very high temperature the Fe^{III} state becomes unstable, and the Fe^{II} state stable, the FeCl_3 passing spontaneously into FeCl_2 . This is the case with most other elements also; in fact, it is a general phenomenon.

On reflecting on these matters, it occurred to me early in this year that if an increase of atomic weight acts in the same way as an increase of temperature, would not, conversely, an increase of temperature act in the same way as an increase of atomic weight?

So that if an increase of atomic weight causes non-metals to pass gradually into metals, would not also an increase of temperature produce the same effect?

In other words, would substances that are non-metals at ordinary temperatures assume metallic properties at a very high temperature?

If this be so, a non-metal is nothing more or less than a substance viewed at a temperature *too low* for it to assume metallic properties; and, conversely, a metal is a substance viewed at a temperature *too high* for it to assume non-metallic properties.

So that the metallic and non-metallic conditions are simply *phases*, which all kinds of matter pass through as the temperature increases from zero upwards. If, therefore, we could only cool down a metal, such as copper, to some exceedingly low temperature it would become a non-metal, just as glass is at ordinary temperatures, and refuse to conduct electricity; while, conversely, if we took the non-metallic carbon and heated it up to an excessively high temperature, it would become a metal and conduct electricity.

Of course, this is a mere speculation. But the idea is a

very fascinating one indeed, and, if true, opens out a whole vista of possibilities hitherto scarcely dreamt of.

Moreover, it is contradicted by no known fact. On the contrary, there exist a great and growing number of facts which appear favourable to it. For instance, we all know how enormously the electric conductivity of non-metals increases as the temperature rises. It is sufficient to recall here the enormous increase in the conductivity of the rare earths at a temperature above 800° , a fact which Professor Nernst has utilised in his celebrated lamp. Carbon also increases enormously in conductivity. Professor T. Gray (*Proc. Roy. Soc.*, January 12, 1882) showed that an increase of only 300°C . caused the conductivity of the best insulating flint glass to increase nearly eight-thousand-fold!

Conversely, Callendar and Dewar have established the fact that the electrical resistance of metals does not continue to decrease as the temperature falls, but reaches a small and nearly constant value (Callendar, *Phil. Mag.*, 1899, xlvii., 217), and Lord Kelvin believes (*Phil. Mag.*, March, 1902) that a metal below 1° absolute is a perfect insulator of electricity, at 2° it shows noticeable conductivity, and at 6° it possesses high conductivity; in other words, he thinks that a metal at these low temperatures behaves precisely as a non-metal behaves at ordinary temperatures.

It may of course be objected that whereas the resistance of metals at ordinary temperatures steadily increases with rise of temperature, the resistance of non-metals continually diminishes, so that both kinds of matter act in this respect in a directly opposite manner.

But it must be remembered that our experiments in the case of non-metals have as yet been made over very limited temperature ranges. The molecules of metals, for example, at ordinary temperatures consist of only single atoms; whereas those of non-metals consist almost invariably of several atoms bunched together. Before we can expect non-metals to behave like metals, we should have to heat them so highly that they too are reduced to the same molecular condition as metals at ordinary temperatures; and this only occurs at very high temperatures indeed, as Victor Meyer proved in the case of the halogens.

This idea of the mutual convertibility of metals and non-metals might appear at first sight somewhat startling. But this is due in great measure to the fact that we have been educated to regard metals and non-metals as two distinct and discontinuous kinds of matter. Yet this is not the case. Metals and non-metals are not separated by any arbitrary line of demarcation, but shade gradually and imperceptibly into each other. And this seems to proclaim the unity of both kinds of matter. Why, therefore, should they not be mutually inter-convertible?

It must be remembered the history of science is full of the gradual fall of all arbitrary lines of demarcation. For example, before the time of James Thomson the melting-point of ice was thought to be one of the eternal and unchangeable constants of nature. Yet we all know now that, like most other "constants," it is in truth a variable, depending upon the external conditions of temperature and pressure.

So also at the present time, the metallic or non-metallic nature is thought to be an unchangeable characteristic of an element. So that if an element *happens* at ordinary temperatures and pressures to exhibit metallic or non-metallic properties, as the case may be, it will continue to exhibit them under *all* other conditions of temperature and pressure.

Yet such a view is extremely improbable, and it gains nothing in probability when we reflect on the profound and indeed startling way the properties of every element changes with the temperature and pressure. For instance, carbon at ordinary temperatures is a perfectly inactive element. It refuses to combine with any other element, nor will it dissolve even in the strongest acids.

It is, in fact, an inactive body like nitrogen. Yet it

completely changes its nature at a high temperature. At a red or white heat it becomes one of the most chemically active elements known, displacing metals from their combination with oxygen, and freely combining with H, S, and O.

While at the temperature of the electric arc, it attacks indiscriminately the metals, dissolving freely in them to form the somewhat indefinite carbides, much as metals dissolve in each other at low temperatures to form alloys.

Other elements, too, change their nature in a way quite as remarkable; sodium, for example, being quite chemically inactive at -80°C .

With these astonishing modifications in the properties of elements in mind, he would indeed be bold who would venture to deny that it is possible for a non-metal to change into a metal at a high temperature, or a metal into a non-metal at a low temperature.

A theoretical explanation follows directly from the theory of electrons. We must suppose that non-metals possess a greater specific attraction for electrons than metals, both being viewed at a common temperature.

So that in the case of substances which are in a non-metallic state, the temperature at which they are viewed is not sufficient to detach the electrons from their atoms, and cause them to wander freely in the inter-molecular interstices. Whereas, in the case of substances which are in a metallic state, the temperature is high enough.

In the first case (non-metals), an electric current is caused by the movement of electrons and the atoms to which they are attached (electrolytic conduction). Whereas, in the second case, the electrons move independently of the atoms ("metallic" conduction).

An increase of electric tension acts in much the same way as an increase of temperature in detaching electrons from the surfaces of atoms. So that during the passage of a disruptive discharge, a non-metal, such as glass, is converted into a metallic state. An increase of the electric tension, therefore, lowers the temperature at which non-metals pass into metals. The temperature of conversion is lowered to the ordinary temperatures at the point when the dielectric breaks down under the electric strain.

University of Kiel, Nov. 23, 1902.

THE ESTIMATION OF SULPHUROUS ACID BY MEANS OF A TITRATED SOLUTION OF IODINE.

By A. BERG.

IN the year 1887, in a paper on the examination of the estimation of sulphurous acid by Bunsen's method, M. Volhard made a series of careful observations on the reactions produced when solutions of hydriodic acid and sulphurous acid are added together; in such cases a yellow colouration is produced. According to M. Volhard (*Liebig's Annalen*, vol. cxlii., p. 93) this colouration indicates the formation of hydrosulphurous acid. I am unable to agree with this opinion, and from the facts which I am about to describe I am more inclined to adopt the views of M. Péchard. This chemist (*Comptes Rendus*, vol. cxxx., p. 1188), by allowing gaseous sulphurous anhydride to act on dry iodide of potassium, obtained a yellow compound, of which he measured the tension of dissociation, and of which the formula is KISO_2 . M. Péchard is of the opinion that the same compound is produced still when we operate in the presence of water.

For the purpose of proving the presence of hydrosulphurous acid in the yellow solutions, M. Volhard relies on:—(1) The colour; (2) that, according to him, they have reducing powers more strongly marked than in the corresponding solutions of sulphurous acid; they de-

colorise solutions of indigo instantaneously (*Bull. Soc. Chim.*, [3], vol. xxiii., p. 673).

It is easy to see that the solution of hydrosulphurous acid, such as is obtained by shaking up a solution of sulphurous acid with zinc, is of a reddish-yellow, and not of a greenish-yellow colour like the mixtures of solutions of sulphurous acid and hydriodic acid or iodides.

As for the reducing properties, I have observed that there is a great difference between the solution of hydrosulphurous acid, which decolorises instantly a fairly dark coloured solution of indigo with two or three drops, and the solutions of sulphurous acid treated with hydriodic acid or iodide, which only decolorises it partially, and not sensibly more than does sulphurous acid alone.

To these differences between the two kinds of solutions we can now add one still more important, and that is their action on iodo-mercurate of potassium. Hydrosulphurous acid reduces it immediately when only a small amount is used, and gives a grey precipitate of mercury, while the other solutions are absolutely without action, no matter in what proportion they are used.

The above facts, if they do not enable us to affirm that the yellow colouration is due to the formation of a compound analogous to that obtained by M. Péchard, still entitles us to doubt the presence of hydrosulphurous acid in this aqueous mixture.

There is another point in M. Volhard's work upon which I cannot agree with him; we all know the method of estimating sulphurous acid by means of a titrated solution of iodine devised by Bunsen. We are also aware that this writer only claims accuracy for his method when carried out with very dilute solutions of sulphurous acid (0.03 to 0.04 per cent). With more concentrated solutions the method gives lower figures than we should expect to find theoretically, a fact that Bunsen attributes to the reaction brought about between the sulphuric and hydriodic acids first formed. Several writers have examined this question; most of them have confirmed the irregularities observed by Bunsen without admitting the explanation he gave of the phenomenon; others look upon the method as exact; all agree, however, on this point, namely, that theoretical results are obtained if the sulphurous acid is dropped into the iodine solution instead of the other way about.

After having verified the above irregularities, which, according to his researches, might be as much as a loss of one quarter of the sulphurous acid present in solutions at 2 per cent, Volhard explains the fact by the decomposition, during the titration, of a part of this body into sulphur and sulphuric acid under the influence of the hydriodic acid which is formed. In fact, he has shown that this decomposition would take place according to the following formula: $-3\text{SO}_2 + 2\text{H}_2\text{O} = \text{S} + 2\text{SO}_4\text{H}_2$.

Now, in a research on the same subject (*Bull. Soc. Chim.*, [3], vol. xxiii., p. 499) I became thoroughly convinced of the slowness of this decomposition, since, when we mix solutions of sulphurous acid and hydriodic acid under more favourable conditions than those realised by titration, not less than four or five days elapse before the solution becomes cloudy on account of the precipitation of the first portions of the sulphur. From this it appears to be very improbable that this decomposition could interfere with and falsify the estimation.

Further, will not the two following facts explain the anomalies in a far simpler manner?

(1) Sulphurous acid being oxidisable on contact with the air, this oxidation may take place during the titration; (2) solutions of sulphurous acid, even when dilute, give off a strong odour of this body, which indicates its diffusion into the atmosphere, and consequently its partial disappearance from the solution.

It was on this account that I undertook the examination of Bunsen's method, guarding against these causes of error, and I proceeded in the following manner:—

A Woolf bottle of 500 c.c. capacity was fitted by means of rubber stoppers in the side necks with two burettes

with taps, containing respectively the sulphuric acid to be examined and the titrated solution of iodine. Through the centre neck two tubes were fitted, by which means a current of carbonic acid could be passed through the flask. These tubes were bent three times at right angles outside the flask, their terminal lengths being horizontal, and each one was fitted with a piece of indiarubber tube and a pinchcock; this portion was plunged into boiled water.

After having driven the air out of the apparatus by means of the carbonic acid, the tube through which the gas arrives is closed by screwing up the pinchcock; aspiration is affected by means of the second tube so as to diminish the pressure in the flask sufficiently to allow the liquids in the burettes to run into the flask; finally, the second pinchcock is closed.

We begin by allowing a known volume of the sulphurous solution to run in, then the iodine liquor until there is a little free iodine which does not disappear on prolonged agitation. The whole of the sulphurous acid, both that in solution and that diffused in the atmosphere of the apparatus, has disappeared by this time.

The pinch-cocks are unscrewed, and this allows the boiled water to enter the tubes and drive out the small amount of sulphurous acid which might possibly be there. The excess of iodine is then estimated by means of hyposulphite.

The operation is repeated, but this time a volume of iodine solution is run in first, more than sufficient to oxidise the sulphurous acid which is introduced afterwards. Under these conditions we know that the estimation is correct.

I have used this method with solutions of sulphurous acid of various strengths, and using iodine solutions of different values, according to circumstances, from one-fifth to $\frac{2}{3}$ of an atom of this metalloid per litre.

In the following table the volumes of the titrated solution used are expressed in iodine solution at one-tenth of an atom, or 12.7 grms. per litre, and correspond with 10 c.c. of sulphurous solution:—

Titration, adding the SO ₂ to the I.		Titration, adding the I to the SO ₂ .		
SO ₂ per cent taken.	Volume of iodine solution. C.c.	Time of titration. Minutes.	Volume of I solution. C.c.	SO ₂ per cent found.
0.105	3.27	10	3.35	0.107
0.518	16.2	10	16.0	0.512
0.998	31.2	10	31.3	1.00
1.93	60.2	10	60.4	1.99
		45	60.6	2.06
		10	176.0	5.74
5.62	175.6	45	177.2	6.13

By an examination of the above figures we see that the concordance of the results given by the two methods of working is very satisfactory for concentrations below 1 per cent.

For higher concentrations the agreement is not so close, but curiously enough it is in the opposite direction to what would be expected, more sulphurous acid was found than was actually present in the solution. I have ascertained without any doubt that this is due to the small amount of sulphurous acid which remains between the plug of the glass tap and the tip of the tube, giving off sulphurous acid fumes during the whole time of the titration; this is naturally added to that in the solution used. Again, it may be remarked that the difference is the greater as the time of the titration is longer.

For the purpose of removing this cause of error, I modified the method of working by substituting a sealed tube for the burette containing the sulphurous solution; this tube was drawn out fine at the extremities, and it contained a known weight of the solution under examination. The upper end of the tube was capped with a piece of indiarubber carrying a small pinchcock; owing to the elasticity of the indiarubber stopper, the lower point can

be broken off against the inside of the neck of the flask, after all the air has been driven out of the latter by a current of carbonic acid gas, and a partial vacuum made; the upper point in the indiarubber tube is then broken, and by connecting this latter with the carbonic acid generator and unscrewing the pinchcock the liquid is run into the flask. The operation is then finished as above, taking care at the end to pass some of the boiled water through the drawn-out tube, so as not to lose any trace of sulphurous acid.

In this manner the following results were obtained:—

Pouring the SO ₂ into the I.		Pouring the I into the SO ₂ .		
SO ₂ per cent taken.	Volume of I solution. C.c.	Time of titration. Minutes.	Volume of I solution. C.c.	SO ₂ per cent found.
5.35	167.4	45	167.0	5.34
6.82	213.2	45	213.6	6.83

Thus we see that a very close concordance was obtained between the figure obtained by the two estimations, no matter what the concentration of the sulphurous acid is (up to about 7 per cent), or the time taken up by the titration (up to forty-five minutes).

Thus Bunsen's method gives exact results, if care be taken to exclude the air and to prevent all loss of sulphurous acid by diffusion. There remains to decide to what extent each of these causes of error is responsible.

1. *Oxidation*.—To examine the influence of oxidation, I repeated the same titrations as before, but left the flask full of air. As was to be expected, the figures obtained in this manner varied with the length of the operation and the more or less prolonged shaking up of the solutions. I will only give a few of the results, to show approximately the extent of the discordances observed:—

Pouring the SO ₂ into the I.		Pouring the I into the SO ₂ .		
SO ₂ per cent taken.	Volume of I solution. C.c.	Volume of I solution. C.c.	Loss of SO ₂ per 10 c.c. Grms.	Loss per cent of SO ₂ .
5.62	175.6	170.2	0.0173	3.0
1.98	60.2	58.8	0.0344	2.3
0.998	31.2	30.8	0.0013	1.3

These figures show that the oxidation, while not being negligible, is not the principal cause of the irregularities observed by different writers. I expected to find that this oxidation would be much more important, for if it is the fact that sulphurous acid in solution oxidises slowly in contact with air, I have shown that this oxidation becomes much more rapid in the presence of iodides or of hydriodic acid. To make quite certain of this, it suffices to shake up, in two identical flasks full of air, on the one hand, 10 c.c. of a solution of sulphurous acid, and, on the other hand, the same quantity of the solution treated with 1 grm. of iodide of potassium. After ten minutes, if a salt of barium is poured into each of the flasks, a faint cloudiness is produced in the former, while an abundant precipitate of sulphate of baryta is formed in the latter.

If the above operation is carried out in a graduated test-glass containing a known volume of air, we observe that the absorption of oxygen is about thirteen times as great in the presence of the iodide as in its absence.

This is an interesting phenomenon which I propose to examine further, later on.

2. *Diffusion*.—This is the principal cause of the errors of estimation. To estimate it I placed 10 c.c. of a sulphurous solution, of which the strength was known, in a wide-mouthed conical flask, and for one minute I gave the solution the gyratory movement analogous to that given during titration. After having blown gently into the flask to renew the atmosphere, I rapidly poured the contents as well as the washings with boiled water into an excess of iodine solution. In this manner I obtained the following figures, which again are only approximate:—

Pouring the SO ₂ into the I.		Pouring the SO ₂ into the I, after agitation.		
SO ₂ per cent taken.	Volume of I solution. C.c.	Volume of I solution. C.c.	Loss of SO ₂ per 10 c.c.	Loss per cent of SO ₂ .
5.62	175.6	97.0	0.251	44.7
1.93	60.2	40.6	0.0627	32.5
0.998	31.2	21.8	0.0299	30.0
0.518	16.2	12.4	0.0125	24.1
0.1056	3.30	2.70	0.0019	18.1
0.0423	1.27	1.16	0.0006	13.8

We can see of what great importance is the loss of the sulphurous acid under the above conditions, since it attains almost 50 per cent with solutions at about 6 per cent strength, and is still 14 per cent with very dilute solutions of 0.04 per cent.

Contrary to the hypothesis of M. Volhard, the decomposition of the sulphurous acid into sulphur and sulphuric acid does not interfere in any way with the estimation. The same may be said of the reaction of sulphuric acid on hydriodic acid mentioned by Bunsen. The only causes of error in the estimations are oxidation and diffusion of the sulphurous acid on contact with the air, causes which can be prevented by pouring the sulphurous acid into the iodine solution.—*Bull. Soc. Chim.*, Series 3, vol. xxvii., No. 22.

COMMERCIAL VALUE OF SCIENTIFIC KNOWLEDGE.

RESEARCH CHEMISTS TO BE APPOINTED BY THE GAS LIGHT AND COKE COMPANY.

IN his Presidential Address to the Royal Society, delivered at its annual meeting on December 1st, Sir William Huggins joined the chorus of eminent persons who, during the past year or two, have been endeavouring to impress upon the business men in this country the absolute necessity of a more systematic application of scientific methods, in theory and in practice, to our manufactures and industries. To the plea for increased attention to science in all departments of business, we have from time to time lent whole-hearted support—always giving prominence to the opinion, which we hold very strongly, that in regard to educational reform the impetus necessary in this slow-moving country to bring about any really effective improvement must come from business men, captains of industry. If only employers will (in the language of the advertisements) ask for well-educated employees and see that they get them, the steps necessary for the production of a larger supply of intelligently and usefully educated men will very soon be taken. Then, and only then, will what Sir William Huggins rightly described as "the present inappreciative attitude of our public men, and of the influential classes of society generally, towards scientific knowledge and methods of thought," be radically changed.

Holding this view, we are pleased to give publicity to what we understand is the fact, that the Directors of the Gas Light and Coke Company have recently decided to appoint one or more Research Chemists to carry out investigations and experiments at their extensive chemical works at Beckton, with a view to the more profitable utilisation of the products of coal-tar distillation and the other processes now carried out at these works. This is a very welcome move in the right direction. It has long been a reproach to this country that our German neighbours buy our crude tar products and make enormous profits out of the dyes and other articles of commerce manufactured from these products; and it was only in the October of last year that we devoted several columns of the *Journal of Gas Lighting* to an exposition—first, of the enormous progress of the chemical industries in Germany during the past quarter of a century, and second

of the magnificent system of education which has given Germany the supply of trained chemists which has enabled her to achieve that progress. For the five years 1895-9, three of the largest firms in the dye-manufacturing industry in Germany paid not less than 24 per cent, not less than 26 per cent, and 18 per cent per annum dividends respectively, on capitals amounting in the aggregate to nearly £2,500,000. The total annual production of the German chemical works is now about £50,000,000; and imports are decreasing and exports increasing. Why should this enormous volume of trade and so substantial a percentage of profit from the manufactured articles, for which this country supplies much of the raw material, be allowed to rest quietly in the hands of our German trade competitors? That, apparently, is the question which the Horseferry Road authorities are seeking to answer; and we heartily wish them success in their enterprise, which, as an example to other leaders of industry, is of more value than any amount of talking or writing.

If, however, we are to wrest trade from our rivals, or prevent them from seizing ours, we must learn the lesson from Germany that this is only to be done by paying great attention, and devoting large sums of money, to the provision of facilities for obtaining thorough scientific education. Germany has risen to the first rank in chemical industry by means of the men who have been given thorough instruction, both theoretical and practical, at her Universities and Technical High Schools; and we can only fight science with science. We may repeat the question with which we concluded the articles to which reference has been made: Has this country, has the gas industry, nothing to learn from a consideration of the past successes, the present position, and the future prospects of chemical research in Germany?—*Journal of Gas Lighting*.

American Philosophical Society for Promoting Useful Knowledge.—The success of the General Meeting of the American Philosophical Society, held at Philadelphia last April, has established satisfactorily the claim that the interests of useful knowledge in the United States may be greatly promoted by holding an annual General Meeting of the Society. Such a meeting, not only from the information derived from the papers presented, but also from their discussion, has proved attractive to its members from all parts of the country and has broadened the field of usefulness of this, the oldest scientific society in America. At the concluding session of the General Meeting held last April it was resolved that a second General Meeting be held in April, 1903. In accordance with this resolution the said General Meeting of the Society will take place on Thursday and Friday, April 2 and 3, 1903, and a Committee has been appointed to make the necessary arrangements. Members desiring to present papers, either for themselves or others, are requested to send to the Secretaries at as early a date as practicable and not later than March 1, 1903, the titles of these papers, accompanied by a brief abstract, so that they may be duly announced on the programme which will be issued immediately thereafter, and which will give in detail the arrangements for the meeting. Papers in any department of science come within the scope of the Society, which, as its name indicates, embraces the whole field of useful knowledge. The Publication Committee, under the rules of the Society, will arrange for the immediate publication of the papers presented. The Society by means of its publications, which present a series covering 140 years and include *Transactions* in quarto and *Proceedings* in octavo, with its large exchange list embracing, practically, the scientific societies of the world, and with its exceptional facilities for immediate issue, offers unexcelled avenues for prompt publication and wide circulation of the papers read before it.

CONTRIBUTIONS TO OUR KNOWLEDGE OF
YTTERBIUM.*

By ASTRID CLEVE.
(Continued from p. 287).

III. COMPOUNDS OF YTTERBIUM (continued).

Ytterbium Meta-tungstate, $\text{Yb}_2\text{O}_3 \cdot 12\text{WO}_3 + 35\text{H}_2\text{O}$.

This was obtained from ytterbium sulphate and barium meta-tungstate. The salt crystallises from concentrated solutions in transparent prisms bounded by rectangular surfaces. It is very readily soluble, but is not deliquescent, and, on the whole, is stable in the air.

Analysis of the Pressed Salt.

- 2.2000 grms. of the substance lost 0.1712 grm. over sulphuric acid, and 0.0660 grm. more at 115° . 0.4617 grm. of the residue gave after ignition 0.4390 grm. of the anhydrous salt.
- 0.8571 grm. of the substance on ignition gave up 0.1396 grm. of water, and yielded after treatment with soda 0.0882 grm. Yb_2O_3 and 0.6290 grm. WO_3 .

	Calculated for $\text{Yb}_2\text{O}_3 \cdot 12\text{WO}_3 + 35\text{H}_2\text{O}$, in per cent.		Found.	
	I.	II.	I.	II.
Yb_2O_3 ..	394.2	10.35	83.44	83.86
12WO_3 ..	2784.	73.09	73.39	10.29
$35\text{H}_2\text{O}$..	630.7	16.56	16.29	83.68
	3808.9	100.00		99.97

A completely analogous samarium salt,—



has been prepared by Cleve.

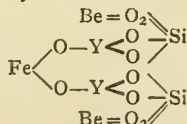
Ytterbium Oxytungstate, $\text{Yb}_2\text{O}_3 \cdot \text{WO}_3 = (\text{YbO})_2 \cdot \text{WO}_4$.

If equivalent quantities of ytterbium oxide and tungstic acid anhydride are ignited in a flux of common salt, only very little action takes place. It is better to act on the earth in presence of larger quantities of WO_3 , but even under these conditions it remains for the most part undissolved. After cooling, the residue is powdered and again ignited with a similar flux. The part that still remains undissolved, after washing with water, was seen to be a mixture of two crystalline salts—a lighter colourless salt, which was separated by washing from the other heavier glittering compact powder, of a faintly reddish grey colour. The latter appeared under the microscope to consist of perfectly-developed short and thick hexagonal prisms with rectangular sections, and sometimes base pyramids. These prisms were analysed.

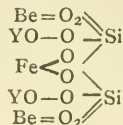
0.8184 grm. of the finely-powdered substance, after protracted treatment with concentrated hydrochloric acid, gave 0.3007 grm. WO_3 , 0.5146 grm. Yb_2O_3 was precipitated in the filtrate by ammonia.

	Calculated for $\text{Yb}_2\text{O}_3 \cdot \text{WO}_3$, in per cent.		Found.
Yb_2O_3 ..	394.2	62.95	62.88
WO_3 ..	232.	37.05	36.74
	626.2	100.00	99.62

The salt represents a type hitherto unknown in the case of the rare earths, $\text{R}^{\text{III}}\text{O}-\text{O}-\text{Y} > \text{R}^{\text{III}}\text{O}_2$; where $\text{R}^{\text{III}}\text{O}$ is a monovalent positive radical, which is of interest inasmuch as it affords an experimental support for the latest formula of gadolinite. The improbability of the older formula suggested by Groth,—



was demonstrated by W. Pettersson ("Studier öfver Gadolinit," *Geol. För. Förh.*, Bd. 12, Hefte 4, p. 70, Stockholm), and this author put forward the following formula:—



Thus, on the assumption that this last formula, which is in any case preferable, is correct, the rare earths occur in nature as the radical $\text{R}^{\text{III}}\text{O}$.

Sodium-ytterbium Tungstates.

1. $2\text{Yb}_2\text{O}_3 \cdot 4\text{Na}_2\text{O} \cdot 7\text{WO}_3$.

This salt was formed at the same time as the preceding, and was obtained from the mixture by washing from the heavier portion. A small quantity also crystallised from the fused mass on cooling. Under the microscope the crystals exhibited a central stem and were developed in two opposite directions in needles with pointed ends. The material, rendered as homogeneous and uniform as possible, was analysed:—

	Calculated for $2\text{Yb}_2\text{O}_3 \cdot 4\text{Na}_2\text{O} \cdot 7\text{WO}_3$, in per cent.		Found.
$2\text{Yb}_2\text{O}_3$..	788.4	29.63	29.44
$4\text{Na}_2\text{O}$..	248.4	9.34	10.61
7WO_3 ..	1624.	61.03	59.91
	2660.8	100.00	99.96

The fact that too high a percentage of sodium was found, and a correspondingly too low percentage of tungstic acid, was due to the difficulty in separating these two substances.

2. $\text{Yb}_2\text{O}_3 \cdot 9\text{Na}_2\text{O} \cdot 12\text{WO}_3$.

This is the probable composition of another double salt which is obtained in small quantity when nearly pure sodium chloride is used as a flux. It forms opaque microscopic needles, insoluble in water.

Analyses.

0.1037 grm. of the substance, treated as above, gave 0.0102 grm. Yb_2O_3 , 0.0750 grm. WO_3 , and 0.0283 grm. NaCl.

	Calculated for $\text{Yb}_2\text{O}_3 \cdot 9\text{Na}_2\text{O} \cdot 12\text{WO}_3$, in per cent.		Found.	Quotients.
Yb_2O_3 ..	394.2	10.55	9.8	1
$9\text{Na}_2\text{O}$..	558.9	14.95	14.5	9.2
12WO_3 ..	2784.	74.50	72.3	12.5
	3737.1	100.00	96.6	

No control analysis could be performed for want of sufficient material. But the numbers found are too low, probably owing to the presence of impurities, as the quotients agree fairly well with the formula suggested.

The double sodium tungstates of the rare earths have been specially examined by Högbom (*Öfv. K. Vet. Ak. Förh.*, Stockholm, 1884, No. 5, p. 111). But attempts to prepare the pure products have as yet been unsuccessful in the case of ytterbium. Neither of the above salts, moreover, belongs to the types put forward by Högbom, which all contain equivalent quantities of acid and basic anhydride. Similarly in the case of the double salt described last, which, on the other hand, is richer in sodium than all hitherto known corresponding compounds in the yttrium group, and in that respect most closely resembles sodium-thorium tungstate, $\text{ThO}_2 \cdot 14\text{Na}_2\text{O} \cdot 16\text{WO}_3$ (Högbom, *loc. cit.*, p. 118). With excess of metallic oxide,

* From the *Zeitschrift für Anorganische Chemie*, xxxii.

Salt *x* forms the transition to the type of the ytterbium oxytungstate.

Ytterbium Formate, $\text{Yb}_3\text{CHO}_2 + 2\text{H}_2\text{O}$
(Dried over Sulphuric Acid).

Forms little needles which unite into hard opaque little balls; very soluble. All water of crystallisation passes off at 100° . A very voluminous oxide remains behind after ignition.

Analyses.

1. 1.1270 grms. of the salt dried over sulphuric acid lost 0.1205 gm. at 130° .
2. 0.7025 gm. of the salt dried over sulphuric acid lost 0.0786 gm. at 100° , and after ignition yielded 0.4000 gm. Yb_2O_3 .

	Calculated for $\text{Yb}_3\text{CHO}_2 + 2\text{H}_2\text{O}$, in per cent.		Found.	
	I.	II.	I.	II.
Yb	173.1	50.30	—	50.02
3CHO_2 ..	135.03	39.23	—	—
$2\text{H}_2\text{O}$..	36.04	10.47	10.69	11.19
	344.17	100.00		

3. 1.2117 gm. of the pressed substance lost at 130° 0.2047 gm., equals 16.84 per cent. For $3\frac{1}{2}\text{H}_2\text{O}$ the calculated value is 16.99 per cent.

Ytterbium Acetate, $\text{Yb}_3\text{C}_2\text{H}_3\text{O}_2 + 4\text{H}_2\text{O}$.

As ytterbium oxide is not soluble in glacial acetic acid, the salt was prepared from the hydrate. It forms small six-sided stable tablets, readily soluble in water. It has a feebly alkaline reaction in solution. At 100° all the water of crystallisation passes off.

Analysis of the Pressed Salt.

- 0.8271 gm. of the substance lost 0.1427 gm. at 110° , and yielded after ignition 0.3829 gm. Yb_2O_3 .

	Calculated for $\text{Yb}_3\text{C}_2\text{H}_3\text{O}_2 + 4\text{H}_2\text{O}$, in per cent.		Found.
	I.	II.	
Yb	173.1	40.99	40.66
$3\text{C}_2\text{H}_3\text{O}_2$..	179.09	41.94	—
$4\text{H}_2\text{O}$	72.08	17.07	17.25
	422.27	100.00	

Specific gravity 2.09
Molecular volume 202.

Ytterbium Propionates.

x. $\text{Yb}_3\text{C}_3\text{H}_5\text{O}_2 + 3\text{H}_2\text{O}$.

Obtained at the temperature of the room in greasy-feeling scales forming spherical aggregations. It gives up no water over sulphuric acid.

Analysis of the Pressed Salt.

1. 0.724 gm. of the substance gave 0.4679 gm. Yb_2O_3 .

	Calculated for $\text{Yb}_3\text{C}_3\text{H}_5\text{O}_2 + 3\text{H}_2\text{O}$, in per cent.		Found.
	I.	II.	
Yb	173.1	38.79	38.32

2. $\text{Yb}_3\text{C}_3\text{H}_5\text{O}_2 + \text{H}_2\text{O}$.

Similar to the former, but separates out at the temperature of water.

Analysis of the Pressed Salt.

1. 0.447 gm. of the substance gave on combustion 0.3620 gm. H_2O , 1.0080 gm. CO_2 , and 0.5054 gm. Yb_2O_3 .

	Calculated for $\text{Yb}_3\text{C}_3\text{H}_5\text{O}_2 + \text{H}_2\text{O}$, in per cent.		Found.
	I.	II.	
Yb	173.1	42.19	42.49
C_3	108.	26.32	25.85
H_{17}	17.17	4.18	3.85
O_7	112.	27.41	—
	410.27	100.00	

Ytterbium Oxalate, $\text{Yb}_2\text{C}_2\text{O}_4 + 10\text{H}_2\text{O}$.

This salt has been described by Nilson (*Ofv. Vet. Ak. Förh., Stockholm*, 1880, No. 6, p. 11). I need only add some determinations of the solubility and specific gravity.

Specific Gravity and Molecular Volume.

- (a). Dried in air ($10\text{H}_2\text{O}$): 1.0769 gm. Specific gravity = 2.644; molecular volume, 299.
- (b). Dried over sulphuric acid: 1.0907 gm. Specific gravity = 2.439; molecular volume, 309.

Solubility of the Oxalate in Ammonium Oxalate

By an experiment carried out according to Brauner's directions ("Contribution to the Chemistry of Thorium," *Trans. Chem. Soc.*, 1898, p. 951), it was proved that 1.2903 gm. crystallised ammonium oxalate (= 1 gm. anhydrous) dissolved in 38.265 gm. of water held in solution 0.02437 gm. Yb_2O_3 at the temperature of the room. Thus, the solubility is about ten times as great as that of yttrium oxalate, for which the corresponding value, according to Brauner, amounts to 0.002562 gm. (Y_2O_3).

Solubility in Normal Sulphuric Acid.

- (a). 100 c.c. normal sulphuric acid were boiled for two hours with excess of ytterbium oxalate. After cooling, the solution required—

	$\text{Yb}_2\text{C}_2\text{O}_4$ Gm.
1. 31.71 c.c. of a chameleon solution equivalent to 0.007424 gm. ammonium oxalate per c.c., corresponding to	0.3857
2. 30.11 c.c. of the same solution, corresponding to	0.3581
Mean	0.3719

- (b). 100 c.c. normal sulphuric acid required after repeated shaking in the cold with excess of ytterbium oxalate 25.09 c.c. of the same permanganate solution corresponding to 0.3053 gm. $\text{Yb}_2\text{C}_2\text{O}_4$.

Hence it follows that, in sulphuric acid also, the solubility is comparatively great, e.g., three to four times as great as that of gadolinium oxalate and about twice as great as that of yttrium oxalate.

Acid Ytterbium Malonate, $\text{YbH}_2\text{C}_3\text{H}_2\text{O}_4$.

Ytterbium hydrate was first dissolved by excess of malonic acid, but the solution soon deposited the above acid salt in fine needles, which were soluble only with great difficulty. The salt after pressing between paper is anhydrous.

Analyses.

1. 0.1548 gm. of the substance dried in the desiccator gave on combustion 0.1078 gm. CO_2 , 0.0181 gm. H_2O , and 0.0812 gm. Yb_2O_3 .
2. 0.2616 gm. of the pressed substance gave 0.1355 gm. Yb_2O_3 .

	Calculated for $\text{YbH}_2\text{C}_3\text{H}_2\text{O}_4$, in per cent.		Found.	
	I.	II.	I.	II.
Yb	173.1	45.78	46.06	45.49
C_6	72.	19.04	18.99	—
H_5	5.05	1.33	1.30	—
O_8	128.	33.85	—	—
	378.15	100.00		

Ytterbium Succinate, $\text{Yb}_2\text{C}_4\text{H}_4\text{O}_4 + 3\text{H}_2\text{O}$.

Succinic acid gives no precipitate with solutions of ytterbium acetate in the cold. If the solution is boiled for a short time, the granular succinate is precipitated. It is soluble only with great difficulty.

Analyses of the Salt Dried in the Desiccator.

- 0.3341 gm. of the substance gave on combustion 0.2368 gm. CO_2 , 0.0690 gm. H_2O , and 0.1758 gm. Yb_2O_3 .

	Calculated for Yb ₂ .3C ₄ H ₄ O ₆ +3H ₂ O, in per cent.		Found.
Yb ₂	346.2	46.26	46.20
C ₁₂	144.	19.24	19.33
H ₁₈	18.18	2.43	2.30
O ₁₅	240.	32.07	—
	748.38	100.00	

*Ytterbium Lactate, Yb₂.3C₃H₅O₃+2H₂O.
(Dried over Sulphuric Acid).*

The addition of lactic acid to ytterbium acetate in the cold caused no turbidity; if the solution is heated, a gelatinous precipitate of the above salt is formed, and may be pressed between paper.

Analysis of the Salt Dried over Sulphuric Acid.

- 0.9128 grm. of the substance suffered a loss in weight of 0.0175 grm. at 100°, equals 1.92 per cent. 0.6444 grm. of the residue gave 0.2684 grm. Yb₂O₃.
- 0.2949 grm. of the substance gave on combustion 0.2505 grm. CO₂, 0.1045 grm. H₂O, and 0.1203 grm. Yb₂O₃.

	Calculated for Yb ₂ .3C ₃ H ₅ O ₃ +2H ₂ O, in per cent.		Found.	
			I.	II.
Yb	173.1	36.34	35.88	35.82
C ₉	108.	22.68	—	23.17
H ₁₉	19.19	4.03	—	3.94
O ₁₁	176.	36.95	—	—
	476.29			

Acid Ytterbium Tartrates.

1. YbH₂.2C₄H₄O₆+12H₂O.

Tartaric acid gives with cold solutions of ytterbium acetate a flocculent precipitate, which, on warming with excess of the acid, again goes into solution. If the tartaric acid is added in exactly sufficient quantity, the acid tartrate crystallises on cooling in needles, which only dissolve with difficulty. A small quantity was crystallised from water and analysed.

- 0.9868 grm. of the pressed salt gave up 0.1366 grm. of water in the desiccator, and 0.1631 grm. more at 110°. 0.6771 of the residue gave 0.2777 grm. Yb₂O₃.
- 0.3248 grm. of the salt dried over sulphuric acid gave 0.1077 grm. Yb₂O₃.

	Calculated for YbH ₂ .2C ₄ H ₄ O ₆ +7H ₂ O, in per cent.	Found.	
		I.	II.
Yb	29.03	29.11	29.12

	Calculated for YbH ₂ .2C ₄ H ₄ O ₆ +12H ₂ O, in per cent.	Found.
5H ₂ O	13.13	13.84 (loss of wt. over sulphuric acid).

2. YbH₂.2C₄H₄O₆+2H₂O (over Sulphuric Acid).

After being kept for some time, a partially crystallised preparation had this composition.

Analysis.

0.7590 grm. of the substance gave on combustion 0.5213 grm. CO₂, 0.1697 grm. H₂O, and 0.2922 grm. Yb₂O₃.

	Calculated for YbH ₂ .2C ₄ H ₄ O ₆ +2H ₂ O, in per cent.		Found.
Yb	173.1	34.19	33.81
C ₈	96.	18.96	18.73
H ₁₃	13.13	2.59	2.50
O ₁₄	224.	44.26	—
	506.23	100.00	

A similar acid yttrium salt (3H₂O) has been prepared by Cleve.

Acid Ytterbium Citrates.

1. 2YbC₆H₅O₇+H₃C₆H₅O₇+12H₂O.

This salt is obtained from ytterbium hydroxide by the addition of just sufficient citric acid to dissolve it. It crystallises from concentrated solutions in little needles which collect together in rays. When dried at 100° the salt is anhydrous.

Analyses.

- 0.6277 grm. of the pressed substance gave up 0.1098 grm. of water in the desiccator; at 110°, 0.0057 grm. more; thus, 0.1155 grm. in all, corresponding to 18.32 per cent. In the given formula are 12H₂O, equals 19.09 per cent.
- 0.4492 grm. of the substance dried at 100° gave 0.1948 grm. Yb₂O₃.
- 0.5122 grm. of the substance dried at 100° gave 0.2221 grm. Yb₂O₃.

	Calculated for 2YbC ₆ H ₅ O ₇ +H ₃ C ₆ H ₅ O ₇ in per cent.	Found.	
		I.	II.
Yb ₂ O ₃	37.78	38.08	38.08

2. 2YbC₆H₅O₇+H₃C₆H₅O₇+15H₂O.

This formula gives the amount of water combined when the substance is kept in an atmosphere saturated with moisture.

Analysis of the Pressed Salt.

0.8907 grm. of the substance gave up 0.1994 grm. of water at 100°, equals 22.37 per cent. According to the above formula, the percentage of water calculated for 15H₂O is 22.77 per cent.

Ytterbium Benzoate, Yb₂.3C₇H₅O₂.

Results as a granular precipitate on bringing together solutions of ytterbium acetate and benzoic acid. It is soluble with very great difficulty in boiling water. The salt is anhydrous, and can be heated to 130° without loss of weight.

Analysis of the Crystallised Salt.

0.2405 grm. of the substance gave 0.0890 grm. Yb₂O₃.

	Calculated for Yb ₂ .3C ₇ H ₅ O ₂ , in per cent.	Found.
Yb	32.28	32.50

Ytterbium Picrate, Yb₂.3C₆H₂(NO₂)₃O+8H₂O.

It forms long perfectly developed columns. The salt is readily soluble, slowly effloresces in the air, and dissolves at about 80° in its water of crystallisation. On heating more strongly, it explodes. Half of the water passes off over sulphuric acid, and the rest at 100°.

Analyses.

- 2925 grm. of the pressed substance gave off 0.0434 grm. of water at 100°.
- 0.3643 grm. of the pressed substance gave up 0.0274 grm. of water over sulphuric acid, and 0.0272 grm. more at 100°.
- 0.2714 grm. of the salt dried at 100° gave, on precipitation with ammonia, 0.0611 grm. Yb₂O₃.

	Calculated for Yb ₂ .3C ₆ H ₂ (NO ₂) ₃ O+8H ₂ O, in per cent.		Found.		
			I.	II.	III.
Yb	173.1	17.28	—	—	16.84
3C ₆ H ₂ N ₃ O ₇	684.42	68.32	—	—	—
4H ₂ O	72.08	7.20	14.40	7.52	—
4H ₂ O	72.08	7.20	—	7.47	—
	1001.68	100.00			

Specific Gravity and Molecular Volume.—0.3238 grm. substance. Specific gravity, 1.95; Molecular volume, 513.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, Thursday, December 4th, 1902.

Dr. W. H. PERKIN, F.R.S., Vice-President, in the Chair.

MR J. H. RYFFEL was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Francis George Cousins, Queen's Road, London, N.; Archibald Seston Elford, B.A., 9, Keble Road, Oxford; Moungh Tha Huyin, B.A., 18, Mercers Road, London, N.; Maurice Kemp-Welsh, Parkstone, Weybridge, Surrey; Samuel Edward Sibley, 3, Rutland Road, Ilford; Duncan Turner, Elmbank, Broomhouse, near Glasgow.

A ballot for the election of Fellows was held, when the following were declared duly elected:—John Frederick Alder; Alfred Edward Beanes; Herbert Blair; John A. H. Brincker, B.A., M.B.; Vernon Seymour Bryant, B.A.; Thomas Burnell Carmichael; Charles Cockle; James Justinian Drought; Edgar Leeder Edlin, B.A.; Sidney Robert Edmison, B.Sc.; Walter Henry Edwards; George Felix Dudbridge Green; Wilfrid Russell Grimwade, B.Sc.; Edward Gumersall; David Vincent Hollingworth; Alfred Holt, jun., B.A.; Arthur Francis Hosking; Clements F. V. Jackson; Douglas Kennedy Jardine, B.Sc.; John Petty Leather; Frank Austin Liddbury, M.Sc.; Ernest Liotard; Thomas Stratford Logan; Douglas A. MacCallum; William Mann, B.Sc.; John Marsh; Joseph William Mellor, D.Sc.; John Price Millington, B.A., B.Sc.; Beni Madhav Mukerjee; John Phelps, B.A.; Richard Pribram, Ph.D.; Guy Dunstan Ricketts, M.A.; George Archibald Park Ross, M.B.; John William Sampson; Duncan Simpson; Robert Walter Sindall; Leonard Smith; John Seabury Smythe, B.Sc., Ph.D.; Edgar Stansfield, B.Sc.; Walter F. Sutherst, Ph.D.; George Sutherland Thomson; Henry Letheby Tidy, B.A.; Thomas Edward Wallis, B.Sc.; William Carter White; Lyndon Wilson.

Of the following papers, those marked * were read:—

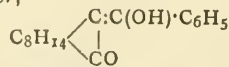
*173. "The Specific Heats of Liquids." By H. CROMPTON.

It is assumed that when heat is applied to a liquid, if there is no change in its molecular composition, (1) there is an increase in the kinetic energy of the molecules, (2) internal work is done within each molecule, (3) there is a diminution in the attraction of the molecules for one another, (4) some external work is done. The last quantity is neglected in considering the specific heat, and the first and second changes are taken to have the same effect on the specific heat of the liquid and on that of its vapour, so that together they make up the specific heat at constant volume of the vapour. At any absolute temperature T , the molecular heat at constant volume of the vapour $C_v = 2.96 + 0.00245 M_{vb} T \log n$, where n is the number of atoms in the molecule, and M_{vb} is the molecular volume of the liquid at the boiling-point. The molecular attraction is regarded as measured by the difference between the latent heat of condensation of the vapour and the heat evolved on simply compressing the vapour into the volume of the liquid without causing a change of state. This attraction is assumed to become zero at the critical temperature, and to increase regularly with the fall in temperature from the critical point downwards. At the absolute temperature T , the change in the attraction is therefore $dA/dT = (L - RT \log V_0/v_0)/(T_k - T)$, in which L is the latent heat of condensation, R the constant of the gas equation, V_0 and v_0 the volumes of the vapour and liquid respectively, and T_k the absolute critical temperature. It follows from the above that the molecular heat of the liquid is $C_f = C_v + dA/dT$, and the author showed that the molecular heats of liquids thus calculated

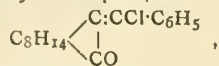
agree fairly with those observed, except where molecular association occurs in the liquid.

*174. "The Constitution of Enolic Benzoylcamphor." By M. O. FORSTER.

From the production of camphorquinone by oxidising benzoylcamphor with chromic acid and with mercuric acetate, it is concluded that the enolic modification of benzoylcamphor has the constitution of *phenylthioxy-methylenecamphor*,—



Phenylchloromethylenecamphor,—



obtained from enolic benzoylcamphor and phosphorus pentachloride, melts at 100° and its rotation $[\alpha]_D = -217^\circ$; the alcoholic solution gives no colouration with ferric chloride. Aniline converts it into *anilinophenylmethylenecamphor anil*, $\text{C}_{29}\text{H}_{30}\text{N}_2$, sulphur-yellow plates, m. p. $117-118^\circ$; the acetyl derivative, $\text{C}_{31}\text{H}_{32}\text{ON}_2$, melts at 166° .

When phenylchloromethylenecamphor is heated with alcoholic ammonia in sealed tubes at $150-170^\circ$, a base having the formula $\text{C}_{17}\text{H}_{21}\text{ON}$ is produced. This melts at 170° , its rotation $[\alpha]_D = +180.2^\circ$; it gives an intense blue colouration with ethereal ferric chloride; the *picrate* melts at 157° , and the *benzoyl* derivative at $99-100^\circ$.

On heating enolic benzoylcamphor with ammonium formate in sealed tubes at $200-220^\circ$, another base, also having the formula $\text{C}_{17}\text{H}_{21}\text{ON}$, is formed. It melts at $118-119^\circ$, its rotation $[\alpha]_D = +235.2^\circ$; it gives no colour with ferric chloride; it does not combine with benzaldehyde or benzoyl chloride, but yields a *picrate* which does not melt at 250° , and a *bromo-derivative*, $\text{C}_{17}\text{H}_{20}\text{ONBr}$, orange-red plates, m. p. 173° .

Enolic benzoylcamphor is reduced in alkaline solution by sodium amalgam, yielding benzylidenecamphor and benzoylcamphor. Potassium permanganate oxidises it to a mixture of benzoic and camphoric acids, whilst potassium ferricyanide gives rise to a compound having the formula $\text{C}_{34}\text{H}_{38}\text{O}_4$ and m. p. 221° , its rotation $[\alpha]_D = +270.4^\circ$; it does not react with ferric chloride, and is insoluble in alkalis.

*175. "Isomeric Benzoyl Derivatives from isoNitrosocamphor." By M. O. FORSTER.

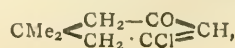
When *isonitrosocamphor* is treated with benzoyl chloride in presence of sodium hydroxide, two compounds are produced each having the empirical formula $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$.

The compound from which *isonitrosocamphor* can be regenerated by hydrolysis, crystallises from alcohol in large, yellow prisms melting at $105-106^\circ$; it is readily soluble in petroleum, and its rotation $[\alpha]_D = +145.6^\circ$ in chloroform. The *isonitrosocamphor* obtained from this derivative has the rotation $[\alpha]_D = +221.9^\circ$, and yields the two new substances on benzoylation.

The compound which accompanies the above-mentioned derivative, although isomeric with it, does not give rise to *isonitrosocamphor* on hydrolysis; it is scarcely soluble in petroleum, and crystallises from alcohol in colourless, lustrous laminæ melting at 136° , and its rotation $[\alpha]_D = +126.9^\circ$ in chloroform. Alcoholic potash resolves it into a mixture of benzoic and cyanolauronic (*α*-camphornitrilic) acids.

*176. "Action of Phosphorus Haloids on Dihydroresorcins. Part I. Dimethyldihydroresorcins." By A. W. CROSSLEY and H. R. LE SUEUR.

Phosphorus trichloride reacts with dimethyldihydroresorcins, giving 5-chloro-3-keto-1 : 1-dimethyl- Δ^4 -tetrahydrobenzene,—



a colourless liquid boiling at 109° (14 m.m.), and also small quantities of an anhydride of dimethyldihydroresorcin, $(C_8H_{11}O)_2O$, melting at 99.5° .

Phosphorus oxychloride gives the same chloroketone, and phosphorus tribromide the corresponding bromo-compound, $C_8H_{11}OBr$, which boils at 129° (25 m.m.).

When phosphorus pentachloride acts on dimethyldihydroresorcin, 3:5-dichloro-1:1-dimethyl- Δ 2:4-dihydrobenzene (*Trans.*, 1902, lxxxi., 826) and 3:5-dichloro-*o*-xylene (*Trans.*, 1902, lxxxi., 1533) are obtained.

By the action of phosphorus pentabromide on dimethyldihydroresorcin, bromodimethyldihydroresorcin is first formed, and the products of the action of the phosphorus bromides on this compound have been investigated. With phosphorus tribromide there is obtained a mixture of mono- and dibromoketodimethyltetrahydrobenzene, the latter, having the formula $C_8H_{10}OBr_2$, melts at 96° ; and a liquid which on treatment with bromine is converted into a tribromoxylene which melts at $175-177.5^{\circ}$. By the further action of bromine the above dibromoketone is converted into tri- and tetra-bromoketodimethyltetrahydrobenzene, which melt respectively at 106° and 118° . These latter substances are also produced by the action of phosphorus pentabromide on bromodimethyldihydroresorcin.

The action of phosphorus pentabromide on dimethyldihydroresorcin is one which is largely influenced by the conditions under which the experiments are carried out. The following products of the reaction have been isolated:—Bromodimethyldihydroresorcin, tribromoketotetrahydrobenzene, a bromoxylene, C_8H_9OBr , melting at $83.5-84^{\circ}$, a dibromoxylene melting at 96.5° , and two tribromoxylens melting at $176-177.5^{\circ}$ and $182-183^{\circ}$ respectively.

177. "The Absorption Spectra of Metallic Nitrates." Part II. By W. N. HARTLEY, D.Sc., F.R.S.

The substances examined were aqueous solutions of the nitrates of fifteen metals, and of nitric, sulphuric, and hydrochloric acids, and alcoholic solutions of ethyl and lithium nitrates.

Metals which exhibit characteristic absorption bands show variations in the positions and intensities of these bands which appear to be dependent upon the molecular weights of the salts in solution. Equivalent quantities of certain metals exhibit the same absorption spectra whether in strong or dilute solution, and, in certain cases, through a great range in dilution. A dilute solution of silver nitrate transmits a longer range of spectrum than a strong solution containing the same quantity of salt. The effect of dilution on nitric acid of sp. gr. 1.42 is the reverse of that observed in the case of silver nitrate. There is a remarkable difference between the constitution of ethyl nitrate on the one hand (whether undiluted or in dilute alcoholic solution), and that of solutions equally dilute of inorganic nitrates on the other. The effect of raising the temperature of the solutions is simply to intensify the absorption spectrum as if a stronger solution at a lower temperature had been used.

Although evidence of what may be regarded as ionic dissociation is afforded by the spectra of dilute solutions of the inorganic nitrates, yet the spectra themselves are not alike, as they would be if the salts were completely resolved into NO_3 and metallic ions; the evidence is just as favourable to the view that some of the salts are resolved into nitric acid and the corresponding base.

In the case of esters, like ethyl nitrate, the conditions are entirely different, as the molecule is clearly not dissociated, there being no evidence of the $-NO_3$ group in the compound.

Views in explanation of the facts observed were put forward.

178. "The Constitution of the Products of Nitration of Meta-acetoluidide." By J. B. COHEN and H. D. DAKIN.

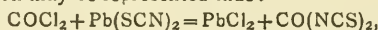
The authors show that the nitro-derivative of meta-acetoluidide obtained by Beilstein and Kuhlberg (*Annalen*, 1871, clviii., 348) contains the nitro-group in the para-

position with respect to the amido-group, and not in the ortho-position as stated by Limpricht (*Ber.*, 1885, xviii., 403). The substance was successively converted into 3-chloro-6-nitrotoluene and 3-chloro-4:6-dinitrotoluene.

By fractional crystallisation from alcohol of the products of nitration, a nitro-derivative which had hitherto escaped observation was separated, which proved to be 4-nitro-3-acetylaminotoluene. On hydrolysis it gave a base identical with the 4-nitro-3-aminotoluene obtained by Staedel and Kolb (*Annalen*, 1890, cclix., 224) by the action of ammonia on 4-nitro-*m*-cresol ethyl ether.

179. "The Action of Metallic Thiocyanates upon Carbonyl Chloride." By A. E. DIXON.

When carbonyl chloride dissolved in toluene is allowed to stand in contact with excess of finely divided sodium, potassium, barium, mercury, or lead thiocyanate, interaction gradually occurs with formation of metallic chloride, and a substance possessing the general chemical characters of a thiocarbimide, but giving, under certain conditions, the reactions of a thiocyanate. It has recently been pointed out by the author that tautomerism of this kind often occurs among the so-called "thiocyanates" of electro-negative radicles (*Trans.*, 1901, lxxix., 541). The interaction may be represented thus:—

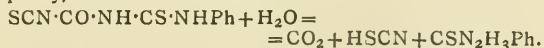


but it does not take place quantitatively, isopropylsulphocyanic acid and pseudo-sulphocyanogen and occasionally other products being formed. Heating to about 100° greatly accelerates the change, but even after thirty hours not more than one-third of the carbonyl chloride employed is converted into thiocarbimide, and much remains unchanged.

Hitherto, all attempts to isolate carbonyldithiocarbimide in a pure state have failed, but its solution interacts with alcohol and with nitrogenous bases, yielding additive products.

Only one molecule of ethyl alcohol could be caused to unite with one of dithiocarbimide; the resultant hemithiourethane, $SCN \cdot CO \cdot NH \cdot CS \cdot OEt$, was obtained in pale yellow prisms melting at $141-142^{\circ}$. It is insoluble in cold water, but decomposes when heated with water to near the boiling-point, carbon dioxide and thiocyanic acid being formed.

By combination with aniline, compounds having either the formula $SCN \cdot CO \cdot NH \cdot CS \cdot NHPh$ or $CO(NH \cdot CS \cdot NHPh)_2$ can be obtained, according to the conditions. The former, carbonylthiocarbimidophenylthiocarbimide, crystallises from alcohol in brilliant, pearly leaflets which melt at 172° , then quickly re-solidify, and now melt at 223° . It is insoluble in cold water but gradually dissolves on boiling, becoming hydrolysed, carbon dioxide being evolved, whilst thiocyanic acid and phenylthiourea remain dissolved:—

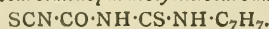


Carbonyldiphenyldithiocarbimide, $CO(NH \cdot CS \cdot NHPh)_2$, separates from alcohol in vitreous prisms which melt at 166° , and are insoluble in boiling water. Both phenylated derivatives, as well as the hemithiourethane, are readily desulphurised by silver salts and by an alkaline lead solution.

Attempts to produce hemi- or complete thiourethanes by adding carbonyl chloride to potassium or barium thiocyanate in alcoholic solution were unsuccessful; the chloride first interacted with the alcohol, yielding ethyl chlorocarbonate, which, with the metallic thiocyanate, gave carboxyethylthiocarbimide, and this latter, combining with another portion of the alcohol, formed finally Doran's carboxyethylthiourethane (*Trans.*, 1896, lxi., 334) or diethyliminodithiocarbonate, $EtO \cdot CO \cdot NH \cdot CS \cdot OEt$.

The following compounds were also described:—

Carbonylthiocarbimidoparatolylthiocarbimide,—



—Pearly leaflets melting at 182° , re-solidifying at once,

and now melting at 237° . In general properties, this and the naphthyl compound mentioned below closely resemble the phenyl homologue. *Carbonyldi-o-tolyldithiocarbamide*, $\text{CO}(\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$.—M. p. 172° , has properties similar to those of the corresponding diphenyl compound. *Carbonylthiocarbimido-a-naphthylthiocarbamide*, $\text{SCN}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, is a yellowish powder, m. p. 182° , re-solidifying at once and then melting at 222° .

Carbonylthiocarbimidophenylbenzylthiocarbamide,—
 $\text{SCN}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NPhBz}$.

—Prepared from benzylniline, it formed long, vitreous prisms having a faint yellow tinge, and melting with effervescence at 180° . When boiled with water it slowly undergoes hydrolysis, carbonic anhydride being evolved, thiocyanic acid passing into solution, and *aa*-phenylbenzylthiourea, $\text{NH}_2\cdot\text{CS}\cdot\text{NPhBz}$, being left.

NOTICES OF BOOKS.

Logarithmic Tables for Chemists. ("Logarithmische Rechen tafeln für Chemiker"). By Professor Dr. Von F. W. KÜSTER. Dritte neu berechnete und erweiterte Auflage. Leipzig, 1902. Pp. 93.

KÜSTER's logarithmic tables for chemists is a really international scientific work, for the main part is written in a language intelligible to all chemists of the civilised world, *in numbers*. Even those who do not understand the short explanation to the tables, will see at once that the quantity of lead corresponding to a found quantity of lead sulphate is obtained by adding to the logarithm of the latter the number 83438. But the tables have another international significance, so far as they offer a practical solution of the question which was for the first time discussed in the light of recent work in the *CHEMICAL NEWS* (1889, lviii., p. 307), *i.e.*, what standard should be used in our chemical calculation. It is true that the oxygen standard ($\text{O}=16$) proposed in this journal has been adopted almost universally by chemists, and especially by the International Atomic Weight Commission; but even those chemists who prefer the hydrogen standard can use the present work, as the quotients give absolutely the same practical results, whichever of the two standards is used.

The arrangement of the tables is very practical, and we may not only commend the book for what is contained in it but also for the many superfluities left out. Table I. gives the atomic weights of elements, which are on the whole identical with those of the international table, but containing now and then a decimal more or less, so that the degree of accuracy of the number is seen at once. Tables II. and III. contain the multiple of the more important atomic weights. Tables IV. and V. the weights of the more important molecules, atomic groups, and equivalents and their multiples. Table VI. contains the quotients used for the calculation of the results of analyses, and we are pleased to find that the author has broken with the old and absurd tradition according to which no notice is taken of the "rare elements" like Be, W, Th, &c., or their compounds. In Table VII. are given useful data for measuring gases. Table VIII. refers to the calculation of "indirect" analyses; whilst Table IX. is a modern one, containing several important physico-chemical constants for the calculation of the molecular weight by any of the three methods. Table X. serves for the calculation of the volume of a vessel by "weighing-out" with water or mercury. Table XI. gives the most important electro-chemical constants; and Tables XII. and XIII. are devoted to solubilities and to a simple direction for preparing normal solutions from the more concentrated ones. After a few pages of explanatory notes to the tables follow tables of five-figure logarithms, and also another table with four-figures for those who are contented with less

accuracy. Both tables may be trusted, as they are free from misprints. But though a modern chemist may be supposed to know the use of logarithms, as they save his time, and do not so easily lead to error as the old-fashioned methods of multiplication or division, yet the chemist who prefers the older mode of calculation will find the ordinary numbers in the tables prominently printed in red type, whereas the logarithmic values are printed in black, so as to avoid confusion. The reviewer and his students have been using Küster's tables for the last seven years with great advantage in the laboratory, and hopes that others will do the same.

BOHUSLAV BRAUNER.

The Chemistry of Perfumes and the Manufacture of Essences. ("Chimie des Parfums et Fabrication des Essences"). By S. PIESSE. With 76 Figures in the Text. Paris: J. B. Baillière et Fils. 1902. Pp. 380.

THIS volume deals with the natural history, chemical composition, and effects of perfumes, and has the advantage of being written by a thoroughly practical man. In this new edition special attention has been paid to artificial perfumes and the preparation of perfumes of known composition.

Perfumes are obtained naturally by expression, distillation, maceration, absorption, and solution; the various processes for carrying out these operations are fully described and illustrated. The third chapter deals with essences, their general characteristic properties, their chemical analysis, and adulteration. For ten years or more chemists have been at work actively in this direction, and a complete account of the facts discovered in this domain will be found in this chapter. The essences are arranged systematically according to the chemical function of the definite compound which plays the principal part in their composition, both from the point of view of their odour and their analysis.

New products are also dealt with, such as synthetic vanilline, artificial musk, ionone, heliotropine, terpineol, &c.

The second part comprises extracts of odours, bouquets, emulsions, pastes, oils, powders, &c.; and finally there is a chapter on substances used in perfumery, such as acetic acid, ammonia, glycerin, vaseline, &c.

A Text-book of Physics. By J. H. POYNTING, D.Sc., F.R.S., and J. J. THOMSON, M.A., F.R.S., &c. Properties of Matter. London: Charles Griffin and Co., Ltd. 1902. Pp. 228.

THE volume on "Sound," by the same authors, has been published already, though it is really the second of the series, of which the present volume on the "Properties of Matter" is the first. These will be followed in due course by others on heat, magnetism, and electricity and light.

These text-books are intended for the use of students who lay most stress on the study of the experimental part of physics, though the greater the mathematical knowledge the student possesses, the easier he will find it to follow all the arguments and reasonings to be found in these pages.

This volume is divided into eighteen chapters, and contains 168 illustrations.

The first few chapters deal with weight, mass, and gravitation, and describe a number of historical experiments by means of which the fundamental laws of gravity were proved. Then follow some half-dozen chapters on elasticity, strain, stresses, torsion, spiral-springs, and impact.

Chapter XI. is on the compressibility of liquids, first established by Canton in the year 1762, and Chapters XII. and XIII. deal with the pressure and volume of a gas, and the thermal effects accompanying alterations in strains.

Capillarity is considered in two chapters, Nos. XIV. and XV., and the diffusion of liquids and gases in the two following ones, while Chapter XVIII. and last is on the viscosity of gases.

The volume is of undoubted value and interest, and as would be expected from such well-known authors, the descriptions and reasonings are clear and easily followed, though in some portions of the work the pages of equations have rather a disconcerting appearance. The book is well printed and provided with a good index.

CORRESPONDENCE.

FIXING NITROGEN FROM THE ATMOSPHERE.

To the Editor of the Chemical News.

SIR,—In reply to the comments of Mr. Ackroyd (CHEMICAL NEWS, vol. lxxxvi., p. 293) on my note on the above subject, I would mention that my concern was for the oxygen,—"fixing nitrogen" being the title of the original paper. I wrote of an annual 12 million tons of nitrate of soda as a serious additional draft on the oxygen of the atmosphere.

I made the amount 5'65 million tons of oxygen from a total of about 1200 billion tons of oxygen in the atmosphere, which is certainly a very small fraction—and small in comparison with that required by a year's coal production. The amount of coal (British and foreign) raised is stated in "Whitaker's Almanac" to have been nearly 700 million tons in the year 1899. Supposing it to have been equivalent to 70 per cent carbon, and to have been burned to equal volumes of CO and CO₂, it would require 980 million tons of oxygen. Coal consumption, too, will for a time increase. Much of the oxygen of the nitrate of soda would, no doubt, eventually re-enter the atmosphere as CO₂ (respiration of animal using plant as food, &c.), and its oxygen be partially recovered by vegetation.

The object of my writing on the subject was to remind that, in the interests of posterity, our capital in oxygen, as well as in fuel, may need to be considered.

Lord Kelvin, at the British Association in 1897, in a paper on the fuel supply and air supply of the world, stated (abstract in *Nature*, September 9, 1897, p. 461) that "it followed that the oxygen of the atmosphere resting over Britain is insufficient to burn up the fuel of the country, and the cessation of life may possibly occur by asphyxiation rather than want of fuel."—I am, &c.,

W. H. DEERING.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

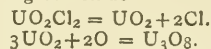
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 21, November 24, 1902.

Ionisation of a Flame containing Salts.—Georges Moreau.—The author finds that the unipolar conductivity of a saline vapour is analogous to that of the mass of hydrogen surrounding a filament of incandescent carbon, or that of the gaseous mass which is in contact with a metal illuminated by ultra violet light. In both these latter cases Thomson discovered the production of negative corpuscles on the surface of contact of the metal and of the gas. For saline vapours it seems natural to suppose that these corpuscles are formed at the contact of a negative incandescent electrode. They are detached from the saline molecules probably by the kinetic energy which they

receive from the surface of the metal. A negative charge accelerates their separation; a positive charge retards it. Such corpuscles thrown into the flame ionise the vapour of the salt in the same way as uranium radiations.

Uranous Oxide.—Echsner de Coninck.—If uranyl chloride is calcined in the air it loses its chlorine and is transformed into a green oxide—



The author repeats this experiment with uranyl bromide, and establishes the fact that, even by prolonging the calcination, similar changes do not take place. Uranyl bromide loses all its bromine, and the radicle UO₂ remains in the form of a brick-red mass, which is stable even at high temperatures. When reduced in a current of pure hydrogen this oxide loses traces of water, and is little by little transformed into the black modification. The author therefore concludes—(1) that the uranous oxide when combined with bromine is first transformed into a brick-red modification and then to a black variety; (2) that uranous oxide which exists in uranyl chloride in the state of a radicle is different, in that it is less stable and is transformed into the green oxide by the action of heat. During the calcination of uranyl bromide the evolution of bromine is very exact and allows of an experimental verification of the molecular weight of uranous oxide and the atomic weight of bromine.

Combinations of Complex Cyanides with the Amines of the Fatty Series.—P. Chrétien.—By saturating ferrohdrocyanic and ferrihydrocyanic acids with the primary, secondary, and tertiary isoamylamines, a series of well crystalline salts are obtained. Ferrohdrocyanic acid, prepared by the usual method, is employed in aqueous or alcoholic solution; the ferrihydrocyanic acid, prepared by the action of sulphuric acid on the barium salt, in aqueous solution. The author successively acts with 1, 2, 3, and 4 molecules of the amine to one molecule of the first acid, and with 1, 2, or 3 molecules to one molecule of the second, and in each case the product is analysed.

Estimation of Glycerin in Wine.—A. Trillat.—The method employed depends on the property which acetic ether possesses, when quite free from all impurities, of dissolving glycerin in the proportion of about 9 per cent at ordinary temperatures, to the exclusion of all the other elements contained in a dry extract of wine.

MISCELLANEOUS.

Two Diaries for 1903.—We have received from the publishers the "Chemists' and Druggists' Diary" and the "Knowledge Diary and Scientific Handbook" for 1903. Besides the usual pages for use simply as a diary, the former contains a great deal of literary matter of interest to chemists and druggists, among which we may mention articles on "Customs Drawbacks," "Excise Licences and Duties," "Formulas for Specialities," "The Medicine Stamp Duty Acts," "Pharmacy and Poison Laws," &c. A number of pages are also devoted to the "Buyer's Guide," which is a complete index to the large number of advertisements in this diary. The "Knowledge Diary" contains, besides a mass of other useful matter, a series of original descriptive articles on various scientific subjects. These include—"Practical Work with the Microscope," by A. Fowler, F.R.A.S.; "Suggestions to Amateur Meteorological Observers," by H. R. Mill, D.Sc.; "Systematic Botany," by R. Lloyd Praeger, B.A.; "Planetary Observation," by W. F. Denning, F.R.A.S.; &c. A very interesting feature of this diary, which we are pleased to see is kept up, is the set of star maps, giving the night sky for one date in every month. There are also maps showing the paths of the planets during the year.

Wilde Gold Medal and Dalton Medal.—The Council of the Manchester Literary and Philosophical Society has awarded the Wilde Gold Medal for 1903 to Professor F. W. Clarke, of the United States Geological Survey, and a Dalton Medal to Professor Osborne Reynolds, F.R.S. In special view of the fact that next year will mark the centenary of the discovery by Dalton of the atomic theory, Professor Clarke (whose writings on the atomic weights are so well known) has also been invited, and has consented, to deliver the Wilde Lecture for 1903. The presentation of the medals and the delivery of the lecture will probably take place in May, 1903.

The Solubility of Salts. Oxalates of Barium.—E. Groschuff.—Neutral oxalate of barium forms several hydrates. That richest in water is the one represented by $C_2O_4Ba + 7/2H_2O$, which occurs in fine needles. The hydrate containing $2H_2O$ is in hexagonal plates of the clinorhombic system; it generally occurs through the action of pure water on the acid oxalate. The hydrate containing $1/2H_2O$ is formed at above 50° ; it resembles closely the two others, in clinorhombic prisms. The monohydrate does not appear to exist. The following is an extract from a table of observed solubilities, giving the number of grms. of C_2O_4Ba dissolved in 1 kilogram. of solution:—

T.	Salts at $7/2H_2O$.	Salts at $2H_2O$.	Salts at $1/2H_2O$.
0°	 0.058	0.053	0.087
18°	 0.112	0.089	0.124
30°	 0.170	0.121	0.140
50°	 —	—	0.164
100°	 —	—	0.211

As for the acid oxalate, $C_2O_4B_2 \cdot C_2O_4H_2 + 2H_2O$ or $+H_2O$ we cannot say for certain that it has a known solubility in water, as it is decomposed by the latter into oxalic acid and the neutral salt, and the reaction is reversible. For example, we get—

T.	Grms. of acid salt decomposed by 100 grms. of water.	Grms. of water necessary to decompose 1 grm. of acid salt.
0°	 1.06	94.7
18°	 2.59	38.6
60°	 14.6	6.85
99°	 46.6	2.15

—*Berichte*, vol. xxxiv., p. 3313.

Oxycelluloses.—A. Nastukoff.—Under the name of β -oxycelluloses, we include those oxycelluloses soluble in ammonia and obtained by the action of nitric acid of 1.3 density on cellulose or on cellulosic materials. By using 2.5 parts of nitric acid, the author obtained a return of 90 per cent; this return diminishes if we increase the amount of acid used, and oxalic acid is then formed. The β -oxycelluloses give a barium salt containing about 5 per cent of barium; this gives us an idea of the molecular size of the β -oxycelluloses, and at the same time enables us to distinguish them from the γ -oxycelluloses, of which the salts of barium contain about 1 per cent of the metal.—*Berichte*, vol. xxxiv., p. 3589.

Autoxidation of Non-saturated Hydrocarbides.—C. Engler and W. Frankenstein.—The fulvenic carbides are particularly susceptible to spontaneous oxidation in the air. Thus, when we make a 5 to 7 per cent solution of dimethylfulvene, $(CH_3)_2C=C_5H_4$, in benzene, and shake it up thoroughly in a flask for several days in contact with air, we observe that the liquid becomes cloudy and then deposits a granular white precipitate; the reaction is helped by light or by a gentle heat. The product formed is a diperoxide with the formula $C_8H_{10}O_4$; it is a white powder, insoluble in most of the organic solvents, and detonating if heated to 130° or with concentrated sulphuric acid, besides being spontaneously decomposable. The same takes place with methylethylfulvene (an orange liquid boiling at 185°); a similar peroxide is formed, but the reaction is less rapid. No definite product of reaction

is produced with cyclopentadiene, nor with hexylene, &c. Experiments in oxidation with all the different carbides in the presence of indigo-carmine, have shown that indigo fixes a quantity of oxygen equal to half that which becomes joined to the carbide.—*Berichte*, vol. xxxiv., p. 2933.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Potassium Persulphate.—(Reply to "S. C.")—"S. C." asks for a method of preparing potassium persulphate; also for probable cause of failure of his own apparatus. The condition necessary for a large and quick yield is a high current density at the anode. The very small current density obtained by using a platinum dish as anode explains the failure of "S. C.'s" apparatus. The writer used for cathode a sheet of platinum-foil rolled into a cylinder inside a cylindrical porous earthenware vessel filled with dilute H_2SO_4 . This was placed in a glass jar containing a saturated solution of $KHSO_4$, in which the anode, a platinum rod, was hung. The whole apparatus was placed in a tin vessel, through which cold water was circulated, and the inner porous cell was cooled by a worm of glass tubing through which cold water ran. A current of 4.5 ampères was used; the temperature being about $12^\circ C$. The persulphate, formed in three to four hours, was filtered off and re-crystallised from hot water; yield, 60 to 70 per cent. With ammonium sulphate the precipitate comes in from fifteen to twenty minutes.—CHAS. S. PATERSON, Chemistry Building, McGill University, Montreal, November 25, 1902.

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THE CHEMICAL NEWS

Vol. LXXXVI., No. 2248.

NOTE OF THE COMPOSITION OF A JERSEY SOIL.

By WILLIAM NAYLOR, F.C.S., A.M.I.C.E.

THE following notes on the chemical composition of a soil from Millbrook, Jersey, Channel Islands, may be worth recording for the use of agricultural chemists who may be called upon in the future to examine soils in this neighbourhood.

The examination was made at the instance of the estate owner, who had reason to believe that it did not respond properly to the variations in the application of nitrogenous and phosphatic manures. This well-defined object of examination, as well as the plainly evident physical character of it—a loamy soil from over a shale formation—rendered any special examination of the moisture absorbing or retentive power, evaporative efficiency, heat absorbing or radiating capacity unnecessary. The sample was drawn this year after the gathering of the potato crop; the particulars of which crop, as well as the manuring, will be given later.

The mechanical examination, after drying four or five days at 80–90° C., gave the following:—

	Per cent.
Coarse gravel, retained by 1/10 inch mesh..	2'322
Consisting of—	
Mineral matter (ammonio-carbonated) ..	2'084
Moisture and organic loss (ignition) ..	0'238
Fine gravel, retained by 1/50 inch mesh ..	6'544
Consisting of—	
Mineral	5'896
Organic	0'648
Fine sand and clay, passed by 1/50 in. mesh	91'134
Consisting of—	
Mineral	83'720
Organic	7'414
Specific gravity	2'441

The slightly higher proportion of loss in the coarser material would be probably due to moisture in the "lumps," for when a representative sample was taken of the air-dried, powdered to pass through a sieve with 2500 holes to the square inch and further dried, the following figures were obtained:—

	Per cent.
Moisture	1'800
Organic matter	6'330
Mineral matter	91'870

For determining the solubility of the mineral residue in acid three separate portions were digested: the first for one day, another during two days, and the last during three days. Hydrochloric acid was used of sp. gr. 1'115.

The differences between each day's figures were but slight after the first day (it was found up to six or seven days); the second of the following three being accepted:—

Matters Soluble in Acid, given as Percentages of the Soil.

	One day.	Two days.	Three days.
Combined silica	0'011	0'012	0'010
Soda (Na ₂ O)	0'101	0'137	0'136
Magnesia (MgO)	0'206	0'180	0'180
Lime (CaO)	0'300	0'350	0'350
Potash (K ₂ O)	0'385	0'340	0'288
Iron and alumina	3'700	3'850	3'500
Phosphoric anhydride ..	0'206	0'206	0'206
Sulphuric anhydride ..	0'154	0'140	0'171
Leaving matters in- soluble	87'030	86'600	86'800

The small quantities of alkalis and alkaline earths present (the whole amounting to only 1 per cent in a humus soil, well manured), is striking, and led to an examination of the soil-producing constituents—the matters insoluble in acids. These, after fusing with alkaline carbonates (barium carbonate separately for the potash estimation), gave the following:—

Matters Insoluble in Acid, as Percentages of the Soil.

Soda and potash	0'000
Magnesia (MgO)	0'250
Lime (CaO)	0'496
Iron and alumina	13'142
Sulphuric anhydride	0'432
Phosphoric anhydride	0'000
Silica	69'905

The proportion of lime and magnesia in the soluble as compared with the insoluble is therefore less, in spite of manuring with superphosphate to the extent of 10 cwts. per acre. Although the insoluble portion evidently affords some small reserve fund of lime and magnesia from which the soil may draw to a slight extent, it is very small, and a sample of the rock formation (shale) was then examined with the object of discovering whether this might afford more. This examination yielded the following figures:—

Soluble in acid—	
Soda (Na ₂ O)	0'239
Potash (K ₂ O)	0'346
Lime (CaO)	0'450
Magnesia (MgO)	0'936
Iron and alumina	9'700
Sulphuric anhydride	0'068
Phosphoric anhydride	0'095
Loss on ignition	4'100
Insoluble in acid	83'450

Of the rock formation, the matter insoluble in acid contained—

Magnesia	0'271
Lime	0'466
Soda and potash	—
Phosphoric anhydride	—
Sulphuric anhydride	0'610
Iron and alumina	25'779
Silica	51'219

It appears clear, then, that the rock formation, in the slow process of disintegration, is likely to afford some little more of the alkaline earths, but not much; and, comparing the tables, it will be noticed that the impoverishment of importance is in respect to lime, magnesia, and soda. By means of the manures used, the potash natural *quantum* is about maintained, while the phosphoric and sulphuric acid figures are augmented.

Although it is well known that, in many cases, it is economical to add more manure than is actually required for plant nutrition, owing to its beneficial action with regard to the moisture-retaining qualities of the soil, its invigorating action on the rootlets or the like, and that any calculation of the actual manure required for absorption based on the ash constituent of the crop is misleading, it may be logical to calculate the *proportions* of nutrient material added and compare them with the ash constituent of the crop, especially where a certain ash constituent of the soil is growing beautifully less.

The following was the manuring of the land in question:—

10 cwt. bone-meal (superphos- phate), equal to	222½ lbs. P ₂ O ₅ 160 lbs. of lime
5 cwt. sulphate of potash, 95 per cent, equal to	287 lbs. K ₂ O 103 lbs. sulphur
7½ cwt. sulphate of ammonia, equal to	203 lbs. sulphur 179 lbs. nitrogen

306

The crop was 12,000 lbs. of potatoes, which pulled very young would have quite doubled if not more than the usual quantity of haum per given weight of tuber. The ash content, then, as compared with the manure added, would be as follows:—

	Ash, lbs. per acre.	Manure applied, lbs. per acre.
Potash	76	287
Lime	48	160
Phosphoric anhydride ..	25	222½
Magnesia	31	—
Soda	7½	—
Sulphur	6½	306
Nitrogen	85	179

(Farmyard manure also added copiously).

Magnesia and lime therefore show up badly—in fact, worst—and in the presence of so much sulphuric acid, in a form not the most easily decomposed. The wash-water from the soil was neutral to litmus. The soluble portion from this sample of soil is compared in the following table with one from a neighbouring estate not so freely manured, but giving better crops—taken after the pulling of the crop. I have reason to believe that, in the latter case, a dressing of chalk is given periodically.

Portion Soluble in Acid.

	Soil No. 1.	Neighbouring estate.
Organic matter	6·330	4·800
Organic nitrogen	0·154	0·112
Sulphuric anhydride ..	0·208	0·000
Phosphoric anhydride ..	0·140	0·066
Potash	0·340	0·231
Soda	0·137	0·071
Lime	0·350	0·500
Magnesia	0·180	0·180

ON CERTAIN TELLURIUM MINERALS, AND THE ACTION OF SULPHUR MONOCHLORIDE THEREON.

By R. W. EMERSON MACIVOR, F.I.C., F.G.C.S., &c.,
Formerly Assistant Professor of Chemistry, Anderson's College
(Medical Faculty), Glasgow.

SULPHUR monochloride readily acts on tellurium with evolution of heat, and according to the proportions in which the two substances are brought together, there results either TeCl or TeCl_4 , and of course free sulphur. Kraft and Steiner, who first studied the reaction (*Berichte der Deut. Chem. Ges.*, xxxiv., 560), by heating two parts S_2Cl_2 with 2·2 parts of tellurium, obtained the black amorphous $\text{TeCl}_4\text{S}_2\text{Cl}_2 + \text{Te} = \text{TeCl}_2 + 2\text{S}$. In this experiment the proportion of Te employed was in excess of that actually required by the equation. But Lenher has shown (*Journ. Am. Chem. Soc.*, xxiv., 189) that, provided an excess of S_2Cl_2 is employed, the Te is converted into the highly crystalline tetrachloride, $2\text{S}_2\text{Cl}_2 + \text{Te} = \text{TeCl}_4 + 4\text{S}$. This reaction takes place at any temperature from the ordinary boiling-point of S_2Cl_2 , viz., 139°C ; the sulphur produced dissolving in the excess of S_2Cl_2 , while the TeCl_4 —which is practically not soluble in the liquid in the cold, though readily so in the heat—separates out on cooling in needle-shaped crystals. Lenher states that the yield of TeCl_4 by this reaction is in nature almost quantitative, and my own results will be seen to quite confirm this opinion.

It occurred to me that it might be not altogether uninteresting to try the action of S_2Cl_2 on the specimen of native tellurium described by me in the columns of the CHEMICAL NEWS some time ago (vol. lxxxii., p. 272), and also on a remarkably pure sample of calaverite from Kalgoorlie, East Coolgardie, W. Australia, kindly sent me two years ago by Mr. Henry Pittman, B.Sc.

The native tellurium had a specific gravity = 6·22, and contained 96·94 per cent of Te and 2·4 per cent of gold. It was first reduced to the finest possible powder, and 2·85 grms. were heated in a large excess of S_2Cl_2 in an open tube for about an hour, when the whole of the Te was found to have been transformed into tetrachloride, and on cooling crystallised out completely. The excess of S_2Cl_2 , containing the dissolved sulphur, was carefully drained off, and the crystals of TeCl_4 thoroughly washed with CS_2 —in which the substance is insoluble—to remove all traces of S_2Cl_2 and S . The tetrachloride obtained had a yellow-grey colour, owing to the impurity in the original mineral—but on volatilising in a current of pure dry CO_2 condensed in beautiful white needles melting at $214\cdot5^\circ$. On testing the small residue left behind in the tube after the complete vaporisation of the TeCl_4 it was found to contain only a mere trace of tellurium.

The calaverite used in these experiments had a specific gravity = 9·314, and consisted of:—

Te	57·00
Au	42·15
Ag	0·60

99·84

Some 4 grms. of the finely-ground mineral were digested in excess of S_2Cl_2 at about 100° , and only after prolonged heating did I succeed in effecting a complete decomposition. The TeCl_4 separated on cooling, and was freed from the S_2Cl_2 and S by decantation and thorough washing with CS_2 . The tetrachloride was dissolved in HCl , the solution filtered, and the Te thrown down by aid of acid sulphite of sodium. The precipitate was collected by reversed filtration on a tared filter, dried at 110°C ., and weighed. I recovered 2·15 grms. of Te , equal to 94·3 per cent of the total amount originally present in the calaverite—a fairly satisfactory result when the circumstances under which I worked are taken into consideration.

The residue left in the tube and on the filter after the extraction of the TeCl_4 by HCl was examined, and found to contain a small amount of tellurium, possibly held in combination by the silver present.

In the course of these experiments I had occasion to make some trials of the various processes for estimating tellurium in the elementary condition, but the results obtained I intend to make the subject of a separate paper.

The Laboratory, 29, Fenchurch Street, E.C.

Sorbic Acid.—O. Dœbner and A. Volf. —Sorbic acid has been prepared by the method already described (*Berichte*, vol. xxxiii., p. 2140) from malonic acid, crotonic aldehyde, and pyridine. **Methylic Ether.**—Prepared from sorbic chloride and methylic alcohol; it is a liquid with an odour of aniseed, boiling at 174° at the ordinary pressure, and at 70° under 20 m.m.; it solidifies in a freezing mixture, and fuses at $+5^\circ$. **Chloride of Sorbyl.**—One part of sorbic acid and two parts of PCl_5 are rubbed up together in a porcelain mortar; the resulting liquid is fractionated under 20 m.m.; chloride of sorbyl boils at 78° under 15 m.m.; the return is from 80 to 85 per cent of the weight of acid used. **Sorbamide.**—Chloride of sorbyl is added drop by drop to aqueous ammonia, concentrated, and cooled with ice. It forms fine needles from a boiling solution in water, or hard prisms from alcohol, fusible at 168° . **Sorbaniide.**—Formed from sorbyl and aniline, fusible at 153° . **Sorbonitrile.**—Two parts of sorbamide and one part of P_2O_5 are heated in an oil-bath at 150° ; it is fractionated *in vacuo*; it occurs as a colourless oil, boiling at 72° under 20 m.m. **Ketone.** $\text{C}_2\text{H}_5\text{—CO—CH=CH—CH=CH—CH}_3$.—Prepared by means of chloride of sorbyl and zinc-ethyl; the product is decomposed by water, and carried off by steam. The ketone is separated from the distillate by the addition of sea-salt; it is a clear, yellow oil, boiling at $90\text{--}95^\circ$ under 26 m.m.—*Berichte*, vol. xxxiv., p. 2221.

ACTION OF TELLURIUM AND SELENIUM ON GOLD AND SILVER SALTS.

By R. D. HALL and VICTOR LENHER.

Historical.

THAT metallic tellurium and selenium act as reducing agents upon solutions of gold and silver salts has been known since the early part of the last century, still their action has not been studied quantitatively.

N. W. Fischer (*Pogg. Ann.*, xii., 502) found that tellurium acts as a reducing agent on salts of gold, silver, platinum, and palladium in solution, the reduction being incomplete in all cases, and that its action on gold solutions is the most rapid, the tellurium after a short time becoming coated with metallic gold, stopping all further action even at a high temperature. Fischer states that the action of tellurium on silver nitrate in solution is slower than on a gold solution, and that the black powder which remains is not silver but a union of tellurium and silver, each in the lowest state of oxidation. He also observes that selenium reduces a gold solution at a high temperature, the action then being the same as that of tellurium, while silver and the remaining metals are not reduced.

Parkham (*Chem. Centrbl.*, xxxiii., 813) found that red selenium is blackened in a solution of silver nitrate, some flakes of selenious acid being formed at the same time; after the latter has been removed by sodium hydroxide the black powder which remains contains both selenium and silver in quantity, but no unchanged selenium is visible under the microscope. He notes that tellurium in a silver nitrate solution gives a black precipitate which shows no metallic lustre under pressure. After digesting tellurium for four days with an excess of a saturated silver nitrate solution he obtained a precipitate, which appeared homogeneous under the microscope, contained both tellurium and silver and no tellurous acid, and concludes that if metallic silver is precipitated by tellurium, then under these conditions nearly all of the tellurium should be in solution. He analysed neither of the precipitates, but he found that selenium in a copper solution gives a precipitate which analysed for Cu_2Se , and that tellurium in a copper solution gives, according to conditions, Cu_2Te or CuTe , and because of this he concludes that selenium in silver solutions forms silver selenide, Ag_2Se , and that tellurium in silver solutions precipitates Ag_2Te , the telluride of silver.

Senderens (*Comptes Rendus*, civ., 175) found that selenium reduces a boiling solution of silver nitrate, either dilute or concentrated, with the formation of silver selenide and selenium dioxide. When the reaction was carried out in a closed tube, he obtained a blue colour which he thought indicated the formation of nitrogen pentoxide. The action of tellurium on a silver nitrate solution was found to be less rapid than that of selenium at 100° but similar to it; also at ordinary temperatures both metals reduce silver nitrate, the action being slow but complete.

Procedure.

The following investigation was undertaken to find out whether gold and silver are precipitated from solutions of their salts by elementary tellurium and selenium. Pure tellurium and selenium were used. They were ground to a powder in an agate mortar and weighed quantities, usually about 0.1 gm., of them kept in contact with the solution of gold or silver for a definite length of time under definite conditions. The precipitate obtained was collected on a Gooch filter, dried at 100° in an air-bath, and weighed; the precipitate was usually tested for either metal that it might contain, and in some cases both the precipitate and the solution were analysed. In most cases solutions containing known quantities of silver and gold were used, so that all the data necessary for an analysis was the determination of the amount of these metals remaining in the solution.

Tellurium in Gold Solutions.

In preliminary experiments on the reducing action of tellurium on solutions of gold chloride, considerable difficulty was first experienced in obtaining results consistent with the equation $3\text{Te} + 4\text{AuCl}_3 = 3\text{TeCl}_4 + 4\text{Au}$, since when tellurium is brought in contact with a gold solution the gold is apt to deposit as a coating on the tellurium, protecting it from all further action, a fact also noted by Fischer. This was in part obviated by grinding the tellurium to an impalpable powder, and even when this was done the tellurium was apt to mass in little balls which it was necessary to crush with a glass rod in order to bring all of the tellurium in contact with the gold solution. That some tellurium not infrequently escaped contact with the gold solution was shown by extracting the precipitate with such solvents as sulphur monochloride and nitric acid. None could be dissolved, showing that the tellurium present was completely enclosed by the gold; but when the precipitate was dissolved in aqua regia, the nitric acid evaporated off and the tellurium and gold precipitated with sulphur dioxide, and this precipitate either tested for tellurium by the above solvents or by fusion with potassium nitrate, invariably where the weight of the precipitate was below that required by the above equation, tellurium could be detected.

It is not necessary that the gold chloride solution should contain more gold than is required by the reaction, for if a large excess of gold solution is used the results are the same, while if an insufficient supply is used it is entirely bleached, all of the gold being deposited. The action of tellurium on gold in solution is fairly rapid; warming a few minutes will bring down sufficient gold to colour the precipitate a decided yellow, yet time is a considerable factor in bringing about complete precipitation, from two to three hours being necessary with continued heating, or several days at room temperatures. The only conditions to be observed, in order to obtain quantitative precipitation of the gold by the tellurium, are sufficient time and the direct contact of all the tellurium with the gold solution.

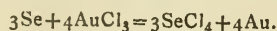
Experiment 1.—0.1010 gm. of tellurium gave 0.2125 gm. of gold; the theory, for total precipitation of the gold by the tellurium according to the equation given, requires 0.2091 gm. The gold solution used contained 0.4346 gm. of gold and was in contact with the tellurium for three hours and was boiled continuously during that time. No test for tellurium could be obtained in the precipitate either before or after dissolving in aqua regia.

Experiment 2.—0.1099 gm. of tellurium gave 0.2257 gm. of precipitate; the theory requires 0.2243 gm. The gold solution contained 0.2351 gm. of gold and was in contact with the tellurium for six days at room temperature. The precipitate contained no tellurium.

Experiment 3.—0.0789 gm. of tellurium gave 0.1642 gm. of gold; the theory requires 0.1635 gm. The precipitate gave no test for tellurium either before or after dissolving in aqua regia.

Selenium in Gold Solutions.

The selenium used was prepared from sublimed selenium dioxide by precipitation with sulphur dioxide in the presence of hydrochloric acid. The selenium was dried, fused, and ground to a fine powder. The fused variety of selenium does not reduce a solution of gold chloride at room temperature. One experiment was made allowing the selenium to remain in contact with the gold solution for three months at room temperature with no visible action. At the boiling temperature the action is nearly as energetic as that of tellurium and is analogous to it, being expressed by the reaction—



The same difficulties were encountered with the selenium as with the tellurium and were overcome in the same way. From six to eight hours of continued boiling are necessary

to insure complete precipitation, or better from two to three days at a temperature of from 70° to 80°.

Experiment 1.—0.0712 grm. of selenium gave 0.2345 grm. of gold, the calculated being 0.2336 grm.

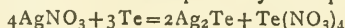
Experiment 2.—0.1058 grm. of selenium gave 0.3455 grm. of precipitate; the theory requires 0.3470 grm. The amount of gold contained in the solution was 0.4346 grm. and it was in contact with the selenium for three days at a temperature of about 80°. The precipitate gave no test for selenium after dissolving and re-precipitating.

Experiment 3.—0.1502 grm. of selenium in a solution of gold chloride boiled for five hours gave 0.4892 grm. of gold; the amount required by the theory is 0.4926 grm.; the precipitate gave no test for selenium.

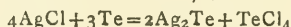
Tellurium in Silver Solutions.

The first salts used were ammoniacal solutions of the nitrate and the chloride of silver. In both cases the solutions were reduced by the tellurium, slowly in the cold and more rapidly if heated, yet tellurium digested with silver nitrate solution for a long time would not completely go into solution leaving metallic silver. Where an ammoniacal solution of silver nitrate was used the weight of the precipitate and the amount of silver in the precipitate was in excess of that required for silver telluride. The amount of silver and tellurium as determined by analysis did not add up to the total weight of the precipitate, and in several cases small plates of metallic silver were formed. On repeating the experiment with no tellurium present it was found that, when silver nitrate stands in contact with ammonia for some time or is warmed with it, a deposit is formed which is insoluble in ammonia. This deposit is probably silver nitride, but when the solution is boiled or kept warm several days the precipitate contains plates of metallic silver. In subsequent experiments the silver nitrate solution was used without ammonia, and the silver telluride formed was removed by washing the precipitate with ammonia.

When silver chloride in ammonia was used, it was allowed to stand in contact with the tellurium at room temperature or only slightly warmed, an excess of ammonia always being present to keep the silver chloride in solution. When the nitrate was used a greater range of temperature was possible, and the solution was either boiled continuously or kept at a temperature of about 80° for a long time. At the end of the experiment the precipitate was collected on a Gooch filter, washed several times with ammonia to remove any silver telluride, and then with water. In this way results were obtained which agree very well with those required by the equation—



where the nitrate of silver is used, and—



where the chloride in ammonia was used. Either the chloride or the nitrate of tellurium would be decomposed by water and would then react with more silver nitrate or chloride to form the telluride of silver.

Experiment 1.—0.1099 grm. of tellurium gave 0.1848 grm. of precipitate; the calculated amount of silver telluride was 0.1978 grm. The solution contained 0.4320 grm. of silver as the chloride and was in contact with the tellurium for eight days.

Experiment 2.—0.1005 grm. of tellurium in a solution of silver chloride containing 0.2160 grm. of silver gave 0.1843 grm. of precipitate, that required for silver telluride being 0.1809 grm.; the time of the experiment was ten days.

Experiment 3.—0.0994 grm. of tellurium in a solution of silver chloride containing 1.0800 grm. of silver gave 0.1767 grm. of precipitate, the calculated for silver telluride being 0.1789 grm. The time of the experiment was three months, and during that time it was kept in a warm place and ammonia added occasionally.

Experiment 4.—0.1018 grm. of tellurium in a solution of silver nitrate which contained 2.0601 grm. of silver gave 0.1871 grm. of precipitate, that required for silver telluride

being 0.1841 grm. The silver remaining in the solution was determined as the chloride and found to be 1.9404 grm., which would make the loss from the solution or the amount of silver in the precipitate as 0.1192 grm. and the amount of tellurium in the precipitate 0.0693 grm. The calculated amount of silver in 0.1871 grm. of the telluride is 0.1178 grm. and the tellurium 0.0693 grm.

The low results in the above series of experiments can be attributed in a large measure to small amounts of tellurium which were so thoroughly enclosed in the mass that they could not be brought to enter into the reaction.

An attempt was made to prepare silver telluride in order to study its properties and compare it with the precipitate obtained from the reduction of the silver solution by tellurium. An excess of aluminum was fused with tellurium and hydrogen telluride evolved from this by treatment with dilute hydrochloric acid. The hydrogen telluride was passed into an ammoniacal solution of silver nitrate in an atmosphere of carbon dioxide to prevent any decomposition of the hydrogen telluride by the oxygen of the air. This gave a black precipitate which was washed repeatedly with water, then dried in an air-bath at 105°. Analysis showed the substance to contain 22.3 per cent tellurium and 77.3 per cent of silver, while the theory for silver telluride requires 37.1 per cent of tellurium and 62.9 per cent of silver. The silver in another sample, prepared in a similar way, was determined by heating the substance in a boat in a current of chlorine gas; the tellurium distilling off as the tetrachloride and the silver chloride remaining was weighed. The per cent of silver obtained in this way was 75.4.

The substance thus prepared fused without loss of tellurium, as was indicated by the absence of fumes, to a porous mass which cut with a metallic lustre. It was acted on by sulphur monochloride, forming tellurium tetrachloride; it reduced a gold solution, depositing metallic gold, but no action could be observed with a silver solution.

The action of hydrogen telluride on silver nitrate may be explained by the decomposition of hydrogen telluride in presence of silver nitrate into nascent hydrogen and tellurium, and these then would reduce the silver solution, the first causing metallic silver to be deposited while the latter would give rise to silver telluride, and this would explain the high percentage of silver.

Silver tellurite was prepared by adding potassium tellurite (obtained by fusion of equivalent weights of tellurium dioxide and potassium carbonate) to a silver nitrate solution; it was dried at 105° and as obtained was a light yellow powder, fairly permanent in the light. Analysis gave 54.95 per cent of silver, while the formula Ag_2TeO_3 require 55.17 per cent. This silver tellurite was reduced by heating it in a porcelain tube to the highest temperature obtainable in the blast-lamp and passing a current of dry ammonia over it for one hour. At the temperature used, tellurium alone would have entirely distilled from the boat. 1.1090 grms. of the silver tellurite were used and 1.0440 grms. of residue obtained; the weight required for silver telluride from the amount of telluride used is 1.0517 grms. The compound obtained by the reduction of the tellurite was analysed by heating in a current of chlorine. 0.2276 grm. gave 0.1908 grm. of silver chloride or 62.65 per cent of silver, the calculated for silver telluride being 62.97 per cent. Another sample of silver tellurite was reduced in carbon monoxide under similar conditions, and the telluride formed was similar in all respects to that obtained by reduction in ammonia.

The silver telluride obtained by the reduction of silver tellurite had a strong metallic lustre, did not tarnish readily, was harder than tellurium, was brittle but not brittle enough to be ground to a powder; it was broken up as finely as possible and treated with sulphur monochloride, gold chloride solution, and silver nitrate solution. Sulphur monochloride acted on it slowly to form tetrachloride; the gold solution was bleached and the silver telluride became coated with gold. 0.2995 grm. was

boiled with a solution of silver nitrate for eight days; at the end of that time the solution gave no test for tellurium, while the particles had lost none of their lustre, showing them to be entirely unacted on.

Brauner (*Fourn. Chem. Soc.*, lv., 388) synthesised silver telluride by fusion of silver in a current of tellurium. He obtained a crystalline mass of metallic lustre having approximately the composition Ag_2Te .

In an Article on the "Naturally Occurring Telluride of Gold" by one of us (*Fourn. Am. Chem. Soc.*, xxiv., 355) specimens of sylvanite, calaverite, coloradoite, kalgoorlite, and nagyagite were treated with a gold solution, and in all cases metallic gold was obtained. Recently some excellent specimens of krennerite, hessite, and more specimens of sylvanite and calaverite were obtained, and as specimens of some of these minerals were not at hand at the time of the previous investigation their action on solutions of gold chloride and silver nitrate was now tried. The minerals examined were:—

One specimen calaverite, Keystone, Boulder Co., Col. (this was one of the original specimens of Genth).

One specimen calaverite and one of sylvanite from Cripple Creek, Col.

Three specimens hessite from Boles, Siebenburgen, Hungary.

One specimen hessite from Tombstone, Arizona.

One specimen krennerite, West Side Mine, Cripple Creek, Col.

One specimen krennerite, Boles, Sidenburgen, Hungary.

All of these minerals reduced gold chloride solution, becoming coated yellow, and where a small quantity of solution was used bleached it, agreeing with the previous results. The hessite was without visible action on the silver nitrate solution even when boiled in it; one specimen of krennerite and one of sylvanite gave a small amount of black powder similar to that obtained from tellurium in silver nitrate solution. Hessite is telluride of silver, which as we have seen is without action on silver solutions, while the others contain both silver and gold with the tellurium, or gold with tellurium, from which it would seem that, while the combination of silver with tellurium is without action on silver nitrate solution, that of gold with tellurium reduces silver nitrate.

In the same article reference was made to the action of tellurium on silver nitrate solution, and conclusions stated which in the light of the facts then at hand seemed correct. It was stated that the action of tellurium on silver solutions is similar to that on gold solutions, though not as complete, metallic silver being formed. The results in this later work show that tellurium in silver solutions forms the telluride of silver and not metallic silver. The error in the former statements arose from the use of ammonia in the solution while it was in contact with the tellurium; it was subsequently found that silver nitrate solution standing for a long time with ammonia, or being heated with it, gives a deposit which contains metallic silver.

Selenium in Silver Solutions.

Selenium reduces a solution of silver nitrate or of the chloride in ammonia, either in the cold or on heating. The action is less rapid than that of tellurium but similar to it, a close approximation to the selenide of silver being formed. Parkham's statement that a precipitate of selenium dioxide is formed is obviously incorrect, as he used aqueous solutions, and selenium dioxide is readily soluble in water. The precipitate that he obtained must have been silver selenite. Senderens' experiment of heating the solution in contact with the selenium in a closed tube was repeated; no difference could be detected in the outcome of the reaction, and no blue colouration was observed.

Experiment 1.—0.1012 grm. of selenium in a solution of silver nitrate for eight days gave 0.2513 grm. of precipitate, the theory requiring 0.2497 grm.

Experiment 2.—0.1047 grm. of selenium in a solution of silver chloride containing 0.4320 grm. of silver, gave 0.2550 grm. of precipitate, the calculated for silver selenide being 0.2590 grm.

Experiment 3.—0.1012 grm. of selenium in a solution of silver nitrate containing 2.4157 grms. of silver gave 0.2468 grm. of precipitate, the theory for silver selenide being 0.2497 grm. After the removal of the precipitate the solution contained 2.2370 grms. of silver, which would make the precipitate contain 0.1785 grm. of silver and 0.0683 grm. of selenium, the calculated amounts for 0.2468 grm. of silver selenide being 0.0666 grm. of selenium and 0.1802 grm. of silver.

The precipitate obtained in Experiment 2 was treated with a solution of gold chloride and reduced it nearly as well as does elementary selenium. The fact that both the telluride and the selenide of silver reduce gold chloride suggested an investigation of the action of the sulphide of silver on solutions of silver and gold. Silver sulphide was prepared by passing hydrogen sulphide into a solution of silver nitrate made alkaline with ammonia, the precipitate washed, dried in an air-bath, and then washed with carbon bisulphide to remove any excess of sulphur. A sample of silver sulphide prepared in this way was boiled with a solution of silver nitrate for seven days and the solution tested for sulphur without any trace being found to be present. The silver sulphide reduced gold chloride solution to metal, readily on warming but only slightly in the cold.

Conclusions.

Tellurium reduces a gold chloride solution completely to metallic gold either in the warm or in the cold, and the only difficulties so far as quantitative precipitation is concerned are mechanical ones. The action of tellurium on silver salts in solution is to reduce them with formation of the telluride of silver, which is still a reducing agent, as it throws out gold from solution. The behaviour of the product obtained is, in all respects, similar to that of the telluride of silver obtained by the reduction of silver tellurite and to that of the native mineral itself.

The action of selenium is similar to that of tellurium, but is not as energetic. Selenium reduces silver solutions in the cold, but has no action on gold solutions unless heated nearly to boiling, the action then being fairly rapid and complete. With silver solutions selenium forms silver selenide, which resembles silver telluride in being a reducing agent to solutions of gold salts, both of them being similar to the sulphide of silver in this respect.—*Journal of the American Chemical Society*, xxiv., No. 10.

CONTRIBUTIONS TO OUR KNOWLEDGE OF YTTERBIUM.*

By ASTRID CLEVE.

(Concluded from p. 302).

IV. ELECTROLYTIC CONDUCTIVITY.

BELOW are given the results of some experiments to determine the electrolytic conductivity of solutions of ytterbium salts, and hence the velocity of migration of the ytterbium ion.

The determinations were made according to Kohlrausch's method; thus the conductivity of salt solutions of different concentrations were ascertained by a Wheatstone's bridge and telephone.

A crystallised sulphate, which was prepared from the purest possible material of atomic weight 173.1, was used for the experiments. Series of solutions of different dilutions were made from four different preparations (I.—IV. in the following table), and each of the numbers given is the mean of several separate determinations. All values are referred to 18°. For the greatest dilutions distilled

* From the *Zeitschrift für Anorganische Chemie*, xxxii.

water with a conductivity of at the most $2.5 \cdot 10^{-6}$ was used in platinum vessels, and the results given have been corrected for the conductivity of the water.

v denotes the volume in litres in which a gram.-equivalent equals 64.86179, of crystallised ytterbium sulphate is contained: λ , the equivalent conductivity at 18° .

v .	λ . Series—				Mean value.	Difference.
	I.	II.	III.	IV.		
3.33	20.9	20.9	20.7	20.4	20.7	14.6
6.67	—	24.7	—	—	24.7	
33.33	35.0	35.4	—	35.4	35.3	26.3
333.3	—	61.7	—	61.5	61.6	
666.7	—	74.1	—	—	74.1	36.4
3333.	—	—	97.1	98.8	98.1	
16667.	—	—	105.1	—	105.1	

The table shows that ytterbium sulphate in dilute solution is partially hydrolysed. Some experiments with litmus also led to the same conclusion; in concentrated solutions of the salt the litmus was pure violet, but on increasing the dilution of the same solutions with pure water the litmus became distinctly reddish.

Unfortunately, so far as I know, the conductivity of yttrium sulphate has not been determined, and thus a direct decisive comparison of the relative basicity of the yttrium and ytterbium hydroxides cannot be made. As regards the lanthanum (Muthmann, *Ber. Deutsch. Chem. Ges.*, xxxi., 1829) and praseodymium (Jones and Reece, *Amer. Chem. Journ.*, xx., 606) salts, certain information, may be obtained, but this does not admit of a direct comparison, for the temperature of the research with the first salt was $+25^\circ$, and for the latter no temperature was stated.

V. SUMMARY.

In all the preceding reactions ytterbium has shown itself to be a purely trivalent element. It forms many compounds specially characteristic of the trivalent metals; of these the following examples may be mentioned:—The gold double chloride, the acid selenite, the potassium double ferrocyanide, the potassium double chromate, the periodate, YbIO_5 , and the basic carbonate, R.OHCO_3 . Even in acid solutions neutral ortho-salts of tri-basic acid, as, for example, the phosphoric acids, are formed. Finally, mention must be made of the existence of organic salts of the type of the acid selenite, such as the acid malonate and acid tartrate, formed from two molecules of a dibasic acid by substitution of three-quarters of the acid hydrogen by the metal.

The close relationship of ytterbium to yttrium is specially apparent in the platinum cyanide. This salt is externally completely similar to the corresponding yttrium compound. There is certainly a discrepancy in the amount of water it contains, which was found to be 18 molecules, while, according to information furnished by Cleve, the yttrium and erbium platinum cyanides crystallise with 21 molecules of water. However, it would be best to make further experiments to prove whether a difference in this respect actually exists. This now appears somewhat improbable, since Benedicks has proved that gadolinium platinum cyanide, containing 18 molecules of water, has both the appearance and the crystalline form of yttrium platinum cyanide.

Ytterbium can thus be classed together with yttrium, erbium, gadolinium, and possibly other metals, which have as yet not been prepared in the pure state, in a natural group, based on the similarity of the platinum cyanides. As far as we can judge at present, ytterbium is most closely allied to erbium among these metals, both as regards the composition of many salts, and the comparatively great solubility of the sulphate.

Brauner ("Contribution to the Chemistry of Thorium," *Trans. Chem. Soc.*, 1898, p. 972) has expressed the opinion that the solubility of the oxalates of rare earths in neutral ammonium oxalate is due to the formation of complex salts, and hence may be taken as an indication of the

relative basicity of the earths, so that a soluble double oxalate is formed in greater quantity the more feebly positive the earth is.

If this is the case, ytterbium is one of the least positive of the metals of the rare earths, and takes its place between thorium and yttrium, *i.e.*, far below praseodymium.

But then it seems strange that both gadolinium and ytterbium form a basic carbonate, R.OH.CO_3 , under conditions which, in the case of yttrium, lead to the formation of the neutral carbonate. According to Brauner's arrangement, gadolinium, which is placed between praseodymium and neodymium, comes long before yttrium, and still more ytterbium, and is thus, from the interpretation which has just been put on these facts, much more strongly positive than these last metals.

On the other hand, evidence can be adduced which points to a comparatively feebly positive character in the case of ytterbium.

We must also take into consideration the decomposition of the nitrate, which begins very readily on heating, and upon which Marignac's method of separation is based. The chloroplatinate has, moreover, the composition $2\text{YbCl}_3 \cdot \text{PtCl}_4 + n\text{H}_2\text{O}$, which differs from the usual type for other rare earths, $\text{RCl}_3 \cdot \text{PtCl}_4 + n\text{H}_2\text{O}$, while the yttrium compound differs in exactly the opposite direction. Finally, must be mentioned the formation of oxy-salts, such as $(\text{YbO})_2\text{WO}_4$ and the comparative indifference of the ytterbium earth towards acids.

ARSENIC IN GLYCERIN.

By J. BOUGAULT.

ALTHOUGH glycerin is intended generally for external application only, a certain proportion is taken internally, often in large doses, either by itself or in various preparations; the presence of arsenic, therefore, should not be tolerated.

Commercially, a considerable quantity of glycerin is used in manipulating wine, and in this connection I am informed the users are on their guard, and every sample of glycerin used is examined carefully and especially for this dangerous impurity.

I myself have had occasion to examine glycerins destined for pharmaceutical purposes, which contained quantities of arsenic corresponding to 3 or even 5 centigrms. of arsenious anhydride per litre. And what gives importance to this observation is the fact that the examination was not of one small sample only, but of several samples taken each time from deliveries of several thousand kilograms.

Pharmacists are liable, therefore, to receive such a class of glycerin, and it is well that they should be warned of this eventuality.

The presence of the arsenic is easily detected without having recourse to the destruction of the organic matter, by precipitation in the form of sulphide. But sulphuretted hydrogen is not a convenient reagent to handle, so I recommend the following method, which is of sufficient sensitiveness, and of which the preparation and use is simple. This reagent is based on hypophosphorous acid, which was prepared some years ago as a delicate test for arsenic by MM. Engel and Bernard (*Comptes Rendus*, 1896, vol. cxxii., p. 390; *Journ. de Pharm. et Chim.*, 1896, [6], iii., p. 413).

Twenty grms. of hypophosphite of sodium are dissolved in 20 c.c. of water, and 200 c.c. of pure hydrochloric acid added of density = 1.17. Chloride of sodium is precipitated; this is filtered off through a plug of cotton-wool.

Five c.c. of the glycerin under examination and 10 c.c. of the reagent are placed in a test-tube; after well mixing this is placed in a boiling hot water-bath. With 0.1 milligram of arsenious anhydride we obtain a brown colouration followed rapidly by a brownish flocculent

precipitate; with 0.02 milligram we still get a distinct brown colouration, which is more easily seen if compared with a similar tube not containing arsenic. Even 0.01 milligram gives a colouration, and after standing for some days a precipitate is visible at the bottom of the tube; but considering only the 0.02 milligram test, it is obvious that we can rapidly detect 4 mgrms. of arsenious anhydride per litre.

The appearance of the precipitated arsenic is very characteristic and a practised eye cannot be deceived; if, however, any doubt did exist, the precipitate could be collected and the presence of arsenic confirmed by the well-known method in the form of arseniate of silver.

It would be also very interesting to know how this arsenic comes to be in the glycerin, but the particulars in my possession do not enable me to solve the question in a very definite manner.

Glycerins for pharmaceutical use are obtained by the distillation of raw products from two different sources:—

1. Glycerins from saponification, which are produced by the saponification of fatty matters by means of lime, under pressure.

2. Glycerins, called lyes, which are residues from the manufacture of soaps. The preparation of the first kind gives no opportunity for the introduction of arsenic. As for those of the second kind, being very alkaline, they have to be saturated, before distillation, with commercial hydrochloric acid, which is always arsenical; it may be that this acid is the source of the arsenic of which a portion would be carried over mechanically during the distillation.

Distilled glycerins are then decolourised with animal black, and then often treated with a small quantity of some product to hide their more or less yellow appearance. I am not able to say with certainty whether these two operations are likely to introduce arsenic into the final product.—*Journ. de Pharm. et Chim.*, Series 6, vol. xv., No. 11.

A METHOD FOR THE PREPARATION OF THE DIPHENYLAMINES.

By RAYMOND VIDAL.

THE formation of simple diphenylamine by heating aniline with its hydrochlorate, in a closed vessel, is effected at a relatively high temperature, and the return is limited.

The same does not hold good in the preparation of the more complex diphenylamines. In fact, it is extremely easy to effect the formation either of dioxidiphenylamine by heating the hydrochlorate of *p*-amidophenol with *p*-amidophenol, or that of amidoxydiphenylamine by heating the hydrochlorate of *p*-amidophenol with *p*-phenylenediamine, or again, that of diamidodiphenylamine by heating the hydrochlorate of *p*-phenylenediamine with this base.

In the second case the hydrochlorate of *p*-amidophenol may be replaced by the hydrochlorate of *p*-phenylenediamine, and the *p*-phenylenediamine by *p*-amidophenol.

It is advisable to carry out these reactions in closed vessels in an oil-bath at a temperature of about 200° for four hours.

The reaction is particularly sharp in the presence of a certain amount of water, about three or four times the weight of the compounds used in the operation; these latter should be used in molecular proportion.

The returns are nearly theoretical. On opening the sealed tube a white crystalline mass is discovered, rapidly turning black in the air, and accompanied by a small quantity of liquid, which may be separated by

draining. It is difficult, even when drying *in vacuo*, to obtain white diphenylamines.

The hydrochlorate of diamidophenol, when heated under the above conditions with *p*-amidophenol or *p*-phenylenediamine, forms trisubstituted diphenylamines, but these latter, more easily changed than the preceding ones, are in the form of a blackish mass, even on the opening of the sealed tube.

Monosubstituted diphenylamines are also obtained by the same method, by heating the hydrochlorates of the aromatic amines, oxyamines, or diamines with the aromatic amines, oxyamines, or diamines themselves.

In fact, the reaction discovered by Girard, limited 'up to the present to the formation of the most simple diphenylamine, takes place more easily with the polysubstituted aromatic amines, and the hydrochlorates of the polysubstituted amines.

This reaction, which gives only mediocre returns, when carried out in open vessels and in the dry state, gives a much larger product in a sealed vessel and in the presence of water. It may be generalised by saying that it occurs, whatever the nature or the position of the functions in the compounds used, and it is also as easy to effect as the process which consists of heating dinitrochlorobenzol-1.2.4 with the polysubstituted aromatic amines.—*Moniteur Scientifique*, Series 4, vol. xvi., Dec., 1902.

THE CONSERVATION OF MATTER.

The balance inculcates thrift and morality generally, and weighing should be so constantly resorted to that it becomes an absolute habit. If Rudyard Kipling could but be persuaded to write a song with the refrain, "Weigh, Weigh, Weigh," which could be hummed by girls during their lessons in practical work in science, as well as sung on State occasions, he would be doing education a great service.—*Prof. Armstrong*.

As Mr. Kipling has not responded to the call, we venture to put forward the following poem, but well-meant, substitute.

WHEN you've used up all the borax, and the beads no longer charm,

When you've made sufficient sulphuretted stench,
Will you kindly drop a rider on the graduated arm
Of the little becker balance on the bench.

You have learnt a lot of symbols, long equations and the rest,

And of these just like a parrot you can chatter,
But have you thought of trying on your own account to test

The Indestructibility of Matter?

Gramme weight—drachm weight—weight of a hundred grains.

(Fifty thousand boys and girls, it's all the same to-day.
Each of them doing his own research, each of them using his brains).

Put the weights in the balance pan and weigh—weigh—weigh!

Oh, argon you have read about, and modestly you own

That you think you're fully able to declare,
With an accuracy limited by paper-space alone,
The percentage composition of the air.

You have seen the rose and jessamine grow climbing 'neath the eaves,

And in autumn heard their leaves fall pitter-patter;
But do you see you're proving, as you burn the faded leaves,

The Indestructibility of Matter?

Red leaf—dead leaf—leaf that is charred and hot,

Leaf of a rose or buttercup,—it's all the same to-day.
Each of them serving to prove the law.—And what's to be done with the shot?

Put it into the balance pan and weigh—weigh—weigh!

* The reagent mentioned above can be used for the detection of arsenic in a large number of pharmaceutical preparations, among which the following are the most prominent:—Phosphate of soda, the various phosphates of lime, hydrochloric and sulphuric acids, &c.

Of your knowledge of your bone and blood's components you are proud.

(No doubt you have a list of them by heart).

You can tell in learned language that would mystify the crowd

How the oxyhæmoglobin plays its part.

But you've seen the grasses growing by the margin of the lake,

And you've watched the browsing herd grow slowly fatter,

Yet have you thought you're proving, when you're lunching off a steak,

The Indestructibility of Matter?

Gramme weight—drachm weight—weight of a hundred grains.

(Fifty thousand boys and girls, it's all the same to-day. Each of them doing his own research, each of them using his brains).

Put the weights in the balance pan and weigh—weigh—weigh!

We have burrowed in the coal pits, we have quarried out the stone,

We have forged a house of iron in the flame.

But the whirl-wind and the rain-cloud they shall reap where we have sown,

Nought shall last of that we builded but the name.

Yet although our work shall perish, though it crumble into dust,

Which the four winds of the heavens freely scatter,

There is evidence convincing in that scattered iron rust Of the Indestructibility of Matter.

Brown rust—town rust—rust from the country gates,

Rust from an old torpedo boat, it's all the same to-day. All of it serving to prove the law.—And what's to be done with the weights?

Put them into the balance pan and weigh—weigh—weigh!

M.S., *Central Gazette*.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, December 12th, 1902.

Mr. S. LUPTON, Vice-President, in the Chair.

Mr. S. W. J. SMITH exhibited and described a Portable Capillary Electrometer.

This instrument is a modification of the form of capillary electrometer which consists of two wide tubes joined by a cylindrical capillary tube which may be horizontal or inclined. The apparatus contains mercury and sulphuric acid of about maximum conductivity suitably distributed in the tubes. A spring key is commonly employed with such an instrument, and keeps the two platinum terminals at the same potential unless the spring is depressed. When the spring is depressed, the terminals are put in contact with the two points, the potentials of which are to be tested for equality. In the instrument shown by the author the two wide tubes are sealed at the top to prevent evaporation of the sulphuric acid. The wide tubes are also joined near the top by another tube which allows free motion of the liquids within the apparatus. With this arrangement the instrument is made air-tight, and can, if desired, be made air-free by exhaustion of the apparatus before sealing. The distribution of the mercury can be altered most easily by means of a third cross piece provided with a tap. To prevent the platinum wires forming the electrodes being wetted by the acid, if the apparatus should accidentally, or during transit, be laid on

its side or turned upside down, the lower ends of the tubes may be slightly constricted above the ends of the platinum terminals. If the terminals consist of amalgamated platinum-foil the constriction is unnecessary. If a spring key is made of brass the contacts frequently become unsatisfactory through surface tarnishing, and if to avoid this the bearing surfaces are made of platinum, the key may be subject to thermo-electric effects. Such a key cannot conveniently be fastened on the same stand as the rest of the instrument, for, unless the stand and the support on which it rests are very rigid, the pressure necessary to depress the spring produces sufficient movement of the meniscus, during the act of depression, to render the detection of minute changes of surface-tension impossible. These difficulties are overcome by using a key consisting of a U-tube closed at one end, communicating at the other with a pneumatic pressure-ball, and containing mercury in the bend. Three platinum wires are fused into the tube, so that by squeezing the ball the same change of contacts is produced as by pressing the lever of an ordinary spring key. This form of key can be extended so that a slight pressure applied to the ball makes it work as an ordinary electrometer-key, and greater pressure reverses the contacts between the terminals and the points under investigation. With such an arrangement the sensitiveness of the instrument is doubled, and by using a microscope magnifying 50 diameters a potential difference of $\frac{1}{100000}$ volt can be detected without difficulty. The instrument, used as a surface-tension galvanometer, is more convenient than an ordinary galvanometer with a magnetic system because there is no suspension, no lamp and scale, and practically no levelling.

Dr. R. T. GLAZEBROOK congratulated the author, and said that workers with the capillary electrometer would appreciate the improvements introduced. He said that the author had given the minimum E.M.F. which the instrument could detect, and asked what was the maximum E.M.F. which could be safely applied. He referred to the advantages of the mercury keys exhibited, and remarked that, by their use, many difficulties were obviated.

Dr. LEHFELDT said the mercury keys were improvements on those used by Professor Onnes. In these keys the contacts were changed by the motion of mercury brought about by tilting. The tubes containing the mercury were exhausted to prevent oxidation.

Mr. SMITH, in reply to Dr. Glazebrook, said that the maximum E.M.F. should not exceed half a volt.

A paper "On Astigmatic Aberration" was read by Mr. R. J. SOWTER.

This paper affords a simple explanation of some of the shadow phenomena observed by Prof. S. P. Thompson in his experimental researches on the aberration of lenses, namely, in those experiments in which the aberration is wholly or in part astigmatic. It is shown that the presence of astigmatic aberration in a non-homocentric pencil is accountable merely for the twist or rotation produced in the shadow or image formed by an object placed in, or moved about in, the pencil. The paper commences with a determination of the equation of a surface bounded by the rays of an astigmatic pencil. The focal lines are taken at right angles to each other, and it is assumed that the bounding surface is generated by an ellipse which moves from the primary to the secondary focal line parallel to itself, and to a plane which is at right angles to a line perpendicular to the two focal lines. The equation to the surface is first obtained in Cartesian co-ordinates and then transformed into an equation containing two variables; one the distance of the cutting plane from the primary focal line, and the other the eccentric angle of a point on the elliptic section obtained by the cutting plane. The author then proceeds to determine the rays or generators of this skew surface, and shows that the general equation of a ray can be expressed by the simple formula $\phi = \text{constant}$, where ϕ is the eccentric angle of any point on the ray. The simplicity of this equation points to an easy

method of constructing a string model of the astigmatic surface. The paper then deals with the shadows produced by an object placed in an astigmatic pencil. A straight wire placed at an angle across the beam and cutting the axis will depict upon a screen placed beyond the secondary focal line a straight-line shadow at a definite inclination. If such a wire is moved, without varying the inclination, from the primary to the secondary focal line, then the shadow twists through 90° . If in an experimental pencil or beam there are astigmatic and spherical aberrations present, then a straight wire placed across the beam and moved about would not cast a straight-line shadow but would cast a distorted shadow, such as a figure S, which would be displaced through an angle, the displacement being due to the astigmatic aberration present in the beam.

Prof. EVERETT asked if the paper dealt with a zone or with the whole of a pencil. He said that generally the focal lines were not at right angle. In the ordinary case of a lens at 45° to the axis of a pencil, the secondary focal region was very narrow, and it was possible to trace a curved line through it and call it the secondary focal line, but this line was not at right angles to the axis of the pencil. Most sections in the primary focal region were closed curves cutting themselves twice.

Dr. R. T. GLAZEBROOK said that much of the author's work was based on the assumption that the focal lines were at right angles. The analysis had been simplified by assuming that the surface is formed by the motion of an ellipse, but he thought this assumption ought to be justified. He showed how the results arrived at in the paper could be obtained more generally without any such assumption.

Mr. PRICE referred to a model similar to the elliptical trammels, but with the grooves in different planes. He said that if two fixed points in a bar were constrained to move along these grooves, then any other point on the bar traced out a surface which had characteristics resembling those of an astigmatic surface.

The AUTHOR, in reply, said that he had made certain assumptions to give a simple explanation of the shadow phenomena observed by Prof. Thompson. The fact that a generator of the surface could be expressed by the equation $\phi = \text{constant}$ rendered this explanation easy. With reference to Prof. Everett's question, he said that the analysis applied to the bounding surface of an astigmatic beam.

Prof. L. R. WILBERFORCE exhibited apparatus for a Lecture Experiment on Gaseous Diffusion.

In Graham's experiments on diffusion through porous septa, the gas experimented upon was contained in a vessel inverted over water, and the pressure was kept approximately atmospheric by applying a counterpoise to the vessel. This adjustment, however, is imperfect owing to the weight of the water displaced by the material of the vessel. Prof. Wilberforce showed that, by suspending the vessel from one arm of a balance rendered suitably unstable by a weight above the central knife-edge, a compensating effect could be introduced, and the pressure kept sensibly constant for a considerable range of motion of the vessel. He pointed out that this device could also be utilised for the measurement of pressure.

A paper on "Vapour-density Determinations" by Prof. Sir W. RAMSAY and Dr. STEELE was read by Sir W. Ramsay.

The accurate determination of the densities of gases has been for long an object to which chemists have paid attention. On the other hand, the densities of vapours has only been roughly estimated, as a means of arriving at a conclusion regarding molecular weights; whilst accurate molecular weights have been deduced from the results of analysis, and from previous determinations of atomic weights. The present paper gives a detailed account of some accurate experiments on the densities of vapours over a large range of pressure carried out by a modification of Gay-Lussac's method. This method has

the advantage that while densities are being determined, compressibilities can, within certain limits, be simultaneously estimated with the same sample of material. Berthelot has shown how a knowledge of the compressibility and density of the more permanent gases can be used to compare their relative weights when, if Avogadro's hypothesis be granted, equal volumes contain equal numbers of molecules. This can be done by assuming the compressibility to be a linear function of the pressure, and calculating the value of p_v at zero pressure. The ratio of the p_v 's will then be the ratio of the densities when equal volumes contain equal numbers of molecules. This method has been applied graphically to the results of the authors' experiments on vapours by plotting as ordinates the pressures, and as abscissæ the values of p_v/T . Where the curve cuts the line of zero pressure the theoretical value of p_v/T has been reached. The evidence goes to show that the densities of certain compounds calculated for zero pressure are not proportional to their molecular weights deduced from the atomic weights of the elements which they contain. This conclusion involves one, or it may be several, of a series of assumptions enumerated in the paper. These assumptions are fully investigated and discussed, and the authors suggest that it may be possible that the atomic weights of the elements depend on the proportion in which they are present in the compounds which contain them.

Prof. EVERETT referred to the work of Regnault and Amagat upon the variation of the product p_v at high pressures.

Dr. A. GRIFFITHS, in commenting on the theoretical basis of the comparison of densities, indicated his lack of confidence in one of the fundamental hypotheses, viz., that the temperature of a given gas depends simply on a single factor, the mean square of the linear velocity of the molecules.

Dr. LEHFELDT asked what standard substance had been employed throughout the investigation, and whether the authors were satisfied that the different graphs of p_v/T all cut the zero-pressure line in the same point. The experiments seemed to be in agreement with Lord Rayleigh's statement that at low pressures p_v/T is a constant for the permanent gases.

Sir W. RAMSAY said that the standard substance used was oxygen, and that the curves obtained for any vapour at different temperatures practically cut the zero-pressure line at the same point.

The Society then adjourned until January 23rd, 1903.

NOTICES OF BOOKS.

The New Volumes of the Encyclopædia Britannica. The Eighth of the New Volumes, being Vol. XXXII. of the Complete Work. London: *The Times*. Edinburgh: Adam and Charles Black. 1902. Pp. 872.

The eighth number of the new volumes comprises those subjects coming within the alphabetical headings P R I (Pribiloff Islands) and S T O (Stowmarket). Though not so rich in items of scientific interest as some of its predecessors, there are still a fair number of articles which call for special notice.

In the first place there is the Prefatory Essay by Karl Pearson, entitled "The Function of Science in the Modern State"; this article is of considerable length and deals with a very complex problem from various points of view. "The future," says the author, "is to the nations which not only realise the international struggle in all fields of activity, but consciously develop all the factors of national efficiency with this end in view. . . . Brute force, strength and bravery, material wealth, have in turn been dominant in the State; to-morrow will be marked by the dominance of intelligence."

The future will be an era of specialism, in which every

one will have to be carefully trained in some particular art, or else not only the individual, but the State, will have to drop out of the struggle of nations. To this end science is becoming more and more the paramount factor, and the proper recognition of science by the State is the most encouraging sign of modern times. The author advocates the formation of a "State Science Counsel," with a patent like that of the existing King's Counsel, as a spur or incentive to young men, and a reward to those who have distinguished themselves; we may point out that the "Order of Merit" recently founded seems to fulfil this requirement to some extent, though the standard has been fixed too high for the "general practitioner" of science.

The article on "Public Health," by A. Wood Renton, is short, but sets forth clearly some of the requirements and provisions of the laws on this subject. "The Theory of Radiation," by Dr. J. Larmor, Sec. R.S., covers nearly eight pages, and, as its title indicates, is essentially of a mathematical character; it deals with the law of distribution of energy, pressure of natural radiation, the temperature of an isolated ray, the temperature of the sun, &c.

"Sewage Disposal," by the late Santo Crimp, M.Inst.C.E., is an article on an important practical subject which is claiming more and more attention every year. The author's principal concern is how to deal with sewage at the outfall so as to render it innocuous; but to do this we must have a clear idea of its composition and the circumstances of its delivery. The best way of disposing of sewage is to let it run direct into the sea, under certain restrictions,—that is if we do not wish to save any of the valuable nitrogenous matter; the sea purifies it rapidly by means of the living organisms with which it (the sea) abounds; but this method of disposal is not always practicable, and recourse must be had to other means, such as precipitation, or the use of bacteria beds and septic tanks. If the beds are properly aerated and of sufficient area, the aerobic organisms establish themselves in prodigious numbers and attack the organic matter, breaking it down into harmless soluble and gaseous products with great rapidity.

"Silver" is dealt with by H. O. Hofman, Ph.D. He describes the various means adopted for extracting silver from its ores, such as amalgamation, including the old "Patio" process, and the more modern though still old "Washoe" process. Roasting, lixiviation, and the different forms and combinations of these methods are also described. The article is on the metallurgy of silver only, and does not touch assaying.

Prof. G. E. Hale, of the Yerkes Observatory, contributes a valuable article on "Spectroscopy," covering ten pages, in which solar and stellar spectroscopy naturally take a prominent place. There are many other articles of great general interest, besides those appealing to individuals devoted to special subjects.

The Year-book of New South Wales. Compiled by the Editor of the "Year-book of Australia," for Circulation by the Agent-General in London. 1903. Pp. 168.

INTENDING emigrants, or even travellers, to Australia will find a good deal of both valuable and interesting information in this "year-book"; it contains matter of all kinds—political, social, commercial, historical, geological, &c.; in fact, there is a little of everything.

We have referred on a former occasion to the diamond industry of New South Wales, and are glad to notice that an increase in the output is expected for the year 1902; the Inverell Diamond Fields Company commenced washing on a large scale about a year ago, and their results will doubtless cause a large increase in the quantity of stones found.

The educational system of this State is established by Acts of the local Parliament dealing with primary and secondary schools and with the University; it is interesting to note that though the number of schools and

the number of pupils enrolled and attending increase in a regular manner, the expense, on the other hand, keeps about the same, or at any rate is not increasing anything like so rapidly as the number of scholars.

Twenty-fifth Annual Report of the Connecticut Agricultural Experiment Station for the Year Ending October 31st, 1901. New Haven, Conn.: The Tuttle, Morehouse, and Taylor Company. 1902. Pp. 446.

THE amount of work done at this experiment station is large and varied; it includes not only the examination of commercial fertilisers, of which 429 samples were analysed, but also that of food products, botanical, horticultural, and entomological work, the improvement of waste lands, &c.

The section on fertilisers covers a wide field, and the review of fertilisers gives some valuable information; the value of fertilisers must naturally vary with the soil, crop, and weather, and widely different results may be expected from different places; as a broad general rule it is true that ground bone, superphosphates, fish scraps, dried blood, potash salts, &c., have a high agricultural value, which is related to their trade value, and to some extent determines the latter; but the rule has many exceptions, and in some instances the two do not correspond at all.

An important investigation is being carried out by Dr. Osborne and Mr. I. F. Harris on the constitution and properties of nucleic acid of the wheat embryo, which promises to give very valuable results; the conclusions they have arrived at so far are given in fourteen paragraphs, which are too lengthy, however, for more than a passing reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxxv., No. 22, December 1, 1902.

The Temperature of Ignition and Combustion of the Three Varieties of Carbon in Oxygen.—Henri Moissan.—The author performs a series of experiments, and finds that in every case the combustion of the different varieties of carbon takes place at temperatures which are higher as the polymerisation of the carbon increases. Diamonds become incandescent in oxygen at 800–875°; graphite, at about 650–700°; and amorphous carbon, between 300° and 500°. But each of these rapid reactions is preceded by a reaction becoming slower as the temperature is lowered from the ignition-point.

Composition of Gaseous Hydrates.—M. de Forcrand.—The author, by means of the general relation $Q/T=30$, determines the composition of certain gaseous hydrates, which composition would be impossible to determine by direct analysis. He first applies his rule to hydrate of chlorine, and finds $\text{Cl}_2 + 7\text{H}_2\text{O}$ for its composition; this being verified by direct analysis. In most other cases the first method only is applicable, because the total heat of solidification of the gaseous molecule is not known. Results are obtained for the hydrates of nitrogen, marsh-gas, carbon dioxide, nitrous oxide, ethylene, acetylene, phosphoretted hydrogen, sulphuretted hydrogen, chlorine, bromine, and several other gases.

Transformation of Pyrophosphoric Acid into Orthophosphoric Acid.—H. Giran.—When pure crystalline pyrophosphoric acid is prepared from the syrupy acid having the theoretical composition $\text{P}_2\text{O}_7\text{H}_4$, and this is kept for some time at a temperature of -10° , the acid crystallises out in little white grains of spheroidal form.

The author measures directly the heat of solution of this crystalline acid:—

$P_2O_7H_4$ crys. + aq. = $P_2O_7H_4$ diss. . . . +7'93 cal.
He then finds the heat evolved during the transformation of solid pyrophosphoric acid (liquid or dissolved) to orthophosphoric, and obtains the following results:—

$P_2O_7H_4$ liq. + H_2O liq. + aq. =
= $2PO_4H_3$ diss. . . . +14'47 cal.

$P_2O_7H_4$ sol. + H_2O liq. + aq. =
= $2PO_4H_3$ diss. . . . +12'35 cal.

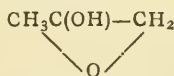
The difference in these two numbers gives the heat of fusion of the pyrophosphoric acid.

Manganese Aluminate.—Em. Dufau.—By means of Moissan's electric furnace alumina and oxide of manganese can easily be made to unite. The author then makes a detailed study of the product, Al_2O_3Mn .

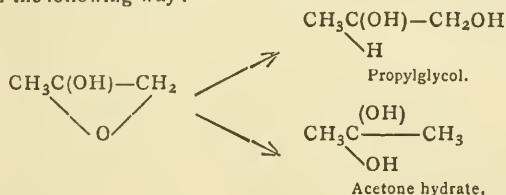
Estimation of Manganese.—H. Baubigny.—It has been previously found that the salts of manganese protoxide can be transformed into those of the insoluble peroxide by the action of certain reagents. The author's investigations on these reactions show that the oxidation of manganese salts by the persulphates takes place only in a very strongly acid medium.

Action of Chlorine and Bromine on the Mononitrated Veratrols.—H. Cousin.—The author determines the constitutional formulæ of a certain number of trisubstituted derivatives of pyrocatechin or its methylic ethers. He also describes two new bodies—a dichlor-3 nitrated veratrol and a dichlor-4-nitrated veratrol.

Hydrogenation of Acetol.—A. Kling.—Free acetol in alkaline, neutral, or acid solutions, whether hot or cold, exists at least partially in a state which has not the usual constitution represented by the formula $CH_3CO.CH_2OH$, but probably by the formula—

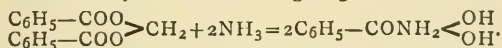


The hydrogenation of this alcohol-ether oxide takes place in the following way:—



The hydrate of acetone is transformed into acetone or its product of hydrogenation—isopropyl alcohol.

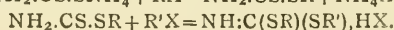
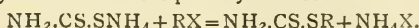
Action of Fatty Amines on Dibenzate.—Marcel Descudé.—The author has already shown that ammonia reacts on methylene dibenzate, giving benzamide,—



This principal reaction is accompanied by two secondary reactions, by which water and formic aldehyde are liberated. From this, ammonium benzoate and hexamethylene tetramine are formed, and no formic aldehyde in the free state. By substituting for ammonia the fatty amines, the reaction is similar; the secondary amines react much less easily than the primary amines, and the tertiary amines have no reaction.

Action of the Halogenated Ethers on Ammonium Thiosulphocarbamate.—Marcel Delépine.—The author studies the action of the halogenated ethers on ammonium thiosulphocarbamate, $NH_2.CS.SNH_4$. One molecule of these ethers produces the thiosulphocarbamic ethers or non-substituted dithiourethanes; a second produces salts of the imido-dithiocarbonic ethers, also non-substituted.

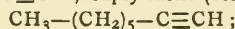
The reactions are similar to those which the author previously describes for the primary amines:—



Bulletin de la Société Chimique de Paris.
Series 3, Vol. xxvii., No. 9.

The Oxides of Molybdenum.—Marcel Guichard.—Already noticed.

Condensation of True Acetylenic Carbides with Formic Aldehyde; General Method for the Synthesis of Primary Alcohols containing an Acetylenic Function.—Ch. Moureu and H. Desmots.—During the condensation of true acetylenic carbides, $R-C\equiv CH$, with formic aldehyde, CH_2O , the authors found a very simple method for the synthesis of primary acetylenic alcohols, $R-C\equiv C-CH_2OH$. Their experiments were carried out on three carbides:— ϵ -Nanthylidene (heptene-1), $CH_3-(CH_2)_4-C\equiv CH$; caprylidene (octene-1),—

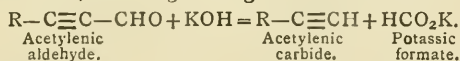


and phenylacetylene, $C_6H_5-C\equiv CH$. After numerous unsuccessful trials, both hot and cold, with commercial formol and carbides in the free state, in the presence of various condensation reagents (potash, hydrochloric and sulphuric acids, and chloride of zinc), they tried the effect of the solid polymer, $(CH_2O)_n$, known as trioxymethylene, on the soda-carbides. These experiments were quite successful. The operation consisted of putting the soda-carbide and the trioxymethylene in contact in the presence of absolute ether, and then decomposing the raw product of the reaction with water. Analysis showed that the new bodies obtained result purely and simply from the addition of the elements of the formic aldehyde, CH_2O , to those of the carbides, $R-C\equiv CH$. They are not precipitated by the reagents of the true acetylenic carbides, $R-C\equiv CH$; for example, nitrate of silver in alcoholic solution has no action on them; thus the active hydrogen of the original true acetylenic carbides has disappeared; and from this it follows that it has been replaced by the alcoholic functional group, which, because of its terminal position, is necessarily primary. Consequently, these compounds must have for their general formula $R-C\equiv C-CH_2OH$, and they are primary alcohols containing an acetylenic function.

Condensation of the True Acetylenic Carbides with the Aldehydes; General Method for the Synthesis of Secondary Alcohols with an Acetylenic Function.—Ch. Moreau and H. Desmots.—Already noticed.

Condensation of the Formic Ethers with the True Acetylenic Carbides. Method for the Synthesis of the Acetylenic Aldehydes.—Ch. Moreau and R. Delange.—Already noticed.

Decomposition of the Acetylenic Aldehydes by the Alkalis.—Ch. Moreau and R. Delange.—Like the acetylenic acetones, the acetylenic aldehydes decompose by hydration under the influence of boiling solutions of the alkalis; there is regeneration of the acetylenic carbide, on the one hand, and production of an alkaline formate on the other, according to the general formula:—



Such, at least, is the equation which represents exactly the phenomenon which occurs with phenylpropionic aldehyde. In the decomposition of amylpropionic aldehyde, $CH_3-(CH_2)_4-C\equiv C-CHO$, it was found that, besides ϵ -Nanthylidene, small quantities of methylamylketone, and even traces of caproic acid, were formed.

Condensation of the True Acetylenic Carbides with the Ether Salts; Methods for the Synthesis of the Acetylenic Acetones and the β -Ketonic Ethers.—Ch. Moureu and R. Delange.—Already noticed.

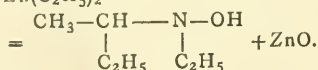
The Extraction of Reducing Sugars (Monoses).—C. Tanret.—The problem of determining the nature of sugars in a mixture, when both hydrolysable sugars and reducing sugars are present, would be much simplified if the mixture could be divided into two portions, one containing the hydrolysable sugars and the other the monoses. The author has attempted to do this by means of phenylhydrazine; theoretically, the monoses must be transformed into phenylhydrazones; these extracted and then decomposed to liberate the sugars. The best means of separating these hydrazones from such a complicated mixture was found to be by shaking them up with acetic ether. The extraction of glucose, levulose, invert sugar, galactose, sorbose, arabinose, &c., is described in detail; but though excellent in theory, this method is less so in practice; part of the sugars is converted into osazones, and another part escapes the reaction altogether, but in spite of all difficulties this method with phenylhydrazine allows from 77.0 per cent (levulose) to 92.0 per cent (glucose) of the monoses to be extracted from a mixture containing them.

Some Iodised Phenols.—P. Brenans.—Already noticed.

Campholenic and Nitro-campholenic Acids; their Constitution.—A. Behal.—A long paper not suitable for abstraction.

MISCELLANEOUS.

Action of Peroxide of Hydrogen on the Fatty Amines.—L. Mamlock and R. Wolfenstein.—Two oxides of triethylamine, $(C_2H_5)_3NO$, have been described; one of them distilling without decomposition is obtained by means of zinc-ethyl and nitroethane; the other is non-volatile, and is obtained by means of hydroxylamine and iodide of ethyl (Dunstan, Golding, *Bull. Soc. Chim.*, vol. xxiv., p. 238; Bewad, Lechman, *Ibid.*, vol. xxiv., p. 792). The authors show that the product of the first reaction is a secondary hydroxylamine, which by reduction gives the secondary ethylbutylamine, $\begin{matrix} CH_3 \\ | \\ CH_3-CH_2 > CH.NH.C_2H_5 \end{matrix}$, and which is formed according to the following equation:—
 $CH_3-CH=NO-OH + Zn(C_2H_5)_2 =$



Analogous experiments have been carried out on the propylic series; *oxide of tripropylamine* (prepared from hydroxylamine or dipropylhydroxylamine, propylate of soda, and iodide of propyl at 65° for two days, or again from tripropylamine and peroxide of hydrogen in cold acetic solution) only exists in the form of the *hydrate*, $(C_3H_7)_3N(OH)_2$, a crystalline mass which re-forms tripropylamine under the influence of PCl_5 , NHO_2 or SO_2 in boiling aqueous solution; the picrate fuses at 130°. Sulphurous anhydride unites with this hydrate at 10°, giving anhydrous oxytripropylsulphamic acid, $(C_3H_7)_3NSO_3$ (a general reaction of tertiary hydroxylamines); it is in the form of silky crystals, fusible at 150°, soluble in the organic solvents with the exception of ligroin, insoluble in water, which, when heated, transforms them into sulphate of tripropylamine; this anhydride is also obtained by passing SO_3 gas through tripropylamine at 0°. Dipropylamine, treated first in the cold and then hot with SO_2Cl_2 , gives the chloride $(C_3H_7)_2NSO_2Cl$, which is transformed by boiling water into dipropylsulphamic acid, $(C_3H_7)_2N SO_3H$, in crystals fusing at 135°, soluble in water and benzene, insoluble in ligroin, identical with the product of the action of SO_2 on dipropylhydroxylamine. Bewad's base (the secondary ethylbutylhydroxylamine) fixes SO_2 in benzenic solution, giving the secondary ethylbutylsulphamic acid, a white amorphous mass, soluble in the usual solvents with the exception of ligroin, fusible at 89–93°; the barium

salt is very soluble in water.—*Berichte*, vol. xxxiv., p. 2499.

New Method for the Preparation of Dehydromucic Acids; its Salts and Ethers.—P. A. Yoder and B. Tollens.—*Preparation.*—Fifty grms. of mucic acid are heated for forty minutes to 133–137° with 100 grms. of H_2SO_4 ; after cooling, 200 c.c. of water are added, and the whole is heated for ten minutes on the water-bath; the next day it is filtered and washed with a little cold water; the impure acid is then dissolved in 800 c.c. of boiling water, and the necessary amount of barytic hydrate added. The solution is filtered, decolourised with charcoal, and finally acidulated with hydrochloric acid, when 12 grms. of dehydromucic acid are deposited. The authors have tried several other methods for its preparation, but have found them all inferior to this one; they have observed in particular, that, contrary to the opinions of Schmidt and Cobenzl, mucate of potash does not give dehydromucic acid when heated. The following salts are described:—*Potassium*, crystalline, with 1.5 or 2 H_2O ; *sodium*, with 4 H_2O ; *ammonium* (anhydrous), in rhombic tables having angles 122.3–122.5°, and 56.9° to 58.6°; *strontium*, with 6 H_2O ; *magnesium*, with 6 H_2O ; *lead*, insoluble in water; *cadmium*, with 4 or 4.5 H_2O ; *copper*, small crystals containing 2.5 or 3 H_2O , and giving pyromucic acid on calcination. The ethers of dehydromucic acid were prepared by the hydrochloric acid method. Their constants are given in the following table:—

	Boiling-point.	Pressure.	Fusing-point.
		M.m.	
Dimethylic ether..	154–156°	15	112°
Diethylic ether..	167–168°	16	47°
Di-n-propylic ether..	177–178°	15	21–21.5°
Di-isopropylic ether..	156–159°	13	42–42.5°
Di-n-butyric ether..	186–189°	13	37–38°
Di isobutylic ether..	172–174°	13	88°
Di-isoamyllic ether..	207–211°	13	37.5°

—*Berichte*, vol. xxxiv., p. 3446.

MEETINGS FOR THE WEEK.

SATURDAY, 27th. } Royal Institution, 3. (Christmas Lectures,
TUESDAY, 30th. } adapted for Young People). "On Locomotion—on the Earth, through the Water, in the Air," by Prof. H. S. Hele-Shaw, LL.D., F.R.S., M.Inst.C.E.
THURSDAY, Jan. 1st. }

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